X-RAY CRYSTALLOGRAPHIC STUDIES OF

FIVE GROUP III COMPOUNDS

by

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B.S., University of Illinois at Chicago Circle, 1970

A THESIS SUBMITTED IN PARTIAL FULFILMENT

OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in the Department

of

CHEMISTRY

We accept this thesis as conforming to

the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

APRIL 1974

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ABSTRACT

Supervisor: Professor James Trotter

The structures of five compounds of group III elements have been determined by single crystal X-ray diffraction, three boron compounds, one aluminum compound, and one gallium compound:

1. $\underline{B},\underline{B}$-diphenylboroxazolidine (2-aminoethyl diphenyl-borinate), $C_{14}H_{16}BNO$.

2. $\underline{B},\underline{B}$-bis($\underline{p}$-fluorophenyl)boroxazolidine, $C_{14}H_{14}BF_2NO$.

3. 4,4-dimethyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-boranatacyclopentane, $C_{15}H_{18}BNO_2$.

4. $\underline{N}$-methyldiethanolaminogallane dimer, $C_{10}H_{24}Ga_2N_2O_4$.

5. ($\underline{pentahapto}$cyclopentadienyl)hydridomolybdenum-μ-dimethylaluminum-μ-[methylaluminum-di-(μ-$\underline{pentahapto}$-($\underline{monohapto}$)cyclopentadienyl)dimethylaluminum]($\underline{pentahapto}$cyclopentadienyl)hydridomolybdenum, $C_{25}H_{35}Al_3Mo_2$.

Crystals of $\underline{B},\underline{B}$-diphenylboroxazolidine are monoclinic, $\underline{a}$ = 13.840(1), $\underline{b}$ = 8.9169(5), $\underline{c}$ = 10.170(1) Å, β = 98.85(1)° , $\underline{Z}$ = 4, space group $\underline{P}2_1/\underline{n}$. The structure was determined by direct methods, and refined by electron-density and full-matrix least-squares procedures to $\underline{R}$ 0.041 for 1458 reflexions. The five-membered boroxazolidine ring is in the half-chair conformation. Bond angles in the ring range from 99.7 for OBN to 110.1° for BOC. Bond lengths are as follows: mean B-C, 1.616(2), B-N, 1.653(3), B-O, 1.484(3), C-N, 1.485(3), C-O, 1.413(3), mean C-C(aromatic), 1.392(11), and

C-C, 1.505(4) Å. The structure consists of discrete molecules linked by O...H-N hydrogen bonds (2.874(2) Å) to form continuous spirals about the 2_1 axes.

Crystals of B,B-bis(p-fluorophenyl)boroxazolidine are orthorhombic, a = 13.442(4), b = 10.214(3), c = 9.823(2) Å, Z = 4, space group $P2_1 2_1 2_1$. The structure was solved by direct methods, and refined by electron-density and full-matrix least-squares procedures to R 0.047 for 1234 reflexions. The five-membered boroxazolidine ring is in a distorted half-chair conformation . Bond angles in the ring range from 99.9(2) for OBN to 108.2(2)° for BOC. Bond lengths are: mean B-C, 1.621(3), B-N, 1.652(4), B-O, 1.471(4), C-N, 1.491(4), C-O, 1.418(4), mean C-F, 1.371(1), mean C-C(aromatic), 1.390(13), and C(sp^3)-C(sp^3), 1.494(6) Å. The structure consists of discrete molecules each linked to six others by an extensive network of O...H-N (O...N = 2.941(3) Å), F...H-N (F...N = 3.171(4) Å), and F...H-C (F...C = 3.318(5) Å) hydrogen bonds.

Crystals of 4,4-dimethyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-boranatacyclopentane are orthorhombic, a = 17.043(3), b = 6.289(1), c = 13.024(2) Å, Z = 4, space group Pna2_1. The structure was determined by direct methods, and was refined by full-matrix least-squares procedures to R 0.071 for 1100 reflexions. Bond angles in the five-membered ring , which has a distorted half-chair conformation, range from 101.5(4) for OBO to 107.1(4)° for NOB. Bond lengths are: mean B-C, 1.632(8), B-O, 1.506(7) and 1.556(8), N-O,

1.409(5), C-O, 1.378(9), C-N, 1.467-1.509(7-10), mean C-C(aromatic), 1.395(25)Å. The structure consists of discrete molecules separated by normal van der Waals distances.

Crystals of the N-methyldiethanolaminogallane dimer are orthorhombic, a = 19.112(4), b = 9.947(2), c = 7.709(2) Å, Z = 4, space group $P2_12_12_1$. The structure was determined by Patterson and Fourier synthesis and was refined by full-matrix least-squares procedures to a final R of 0.056 for 1477 reflexions. The structure provides the first known crystallographic example of pentacoordinate gallium, the dimerization of $MeN(CH_2CH_2O)_2GaH$ occurring via the formation of a four-membered Ga_2O_2 ring. The coordination about the gallium is distorted trigonal bipyramidal with an angle of 151.2(4)° between the axial substituents. The mean bond distances are: Ga-N, 2.192(5), and Ga-O, 2.018(2) for axial ligands; Ga-O, 1.847(2), 1.960(8), and Ga-H, 1.41(4) for equatorial ligands; O-C, 1.419(14), C-N, 1.470(7), C-C, 1.520(12), and C-H, 1.00(13)Å. The molecule has C_2 symmetry to within experimental error. There are possible C-H...O hydrogen bonds (C...O, 3.13(1)-3.44(1)Å) in the structure.

Crystals of the hydridomolybdenum complex, $C_{25}H_{35}Al_3Mo_2$, are orthorhombic, a = 19.398(4), b = 14.438(9), c = 9.035(2) Å, Z = 4, space group $P2_12_12_1$. The structure was determined by Patterson and Fourier syntheses, and refined by full-matrix least-squares procedures to R 0.066 and Rw 0.063 for 1213 reflexions. The molecular structure exhibits several unusual features: C_5H_4 groups which are pentahapto to the

molybdenum atoms and are involved via the unique carbon atom
in multicentre bonding to two aluminum atoms, one of which
occurs as an Al(Me)$_2$ unit and the other an AlMe unit which
also bridges the two molybdenum atoms. The third aluminum
atom is probably involved in a Mo-H-Al(Me)$_2$-H-Mo linkage.
Mean bond distances are: Mo-Al, 2.659 and 2.974, Al-
C(terminal), 2.00, Al-C(bridge), 2.05 and 2.33, Mo-
C(cyclopentadienyl), 2.285, and C-C(cyclopentadienyl), 1.389
Å.

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ACKNOWLEDGEMENTS

GENERAL INTRODUCTION

The historical background and established principles of X-ray crystallography are dealt with in a number of standard texts (1-5). The crystallographic symbols and nomenclature appearing throughout this thesis have their conventional meanings described in the "International Tables for X-ray Crystallography" (6). The main body of the thesis, parts 1-5, consists of the crystallographic studies of the five compounds containing group III elements. Each part includes introductory material relevant to that particular compound as well as details of the structure determination and a discussion of the results.

The final part of the thesis describes a computer program which calculates approximate valence bond orders from observed molecular geometry. It is based on a general relationship which associates bond order with the fractional difference between the observed interatomic distance and the calculated single bond distance. Hybridization and electronegativity effects are considered in the calculation of the single bond distances.

For each of the five crystal structures the least-squares refinement was based on the minimization of $\sum w (F_o - F_c)^2$ where F_o and F_c are the observed and calculated structure factors and w is the assigned weighting factor. The anisotropic thermal factors employed in the refinement are U_{ij} in the expression:

$$f = f^0 \exp[-2\pi^2 (U_{11} h^2 a^{*2} + U_{22} k^2 b^{*2} + U_{33} \ell^2 c^{*2}$$

$$+ \ 2U_{12}hka*b* \ + \ 2U_{13}h\ell a*c* \ + \ 2U_{23}k\ell b*c*) \ ]$$

where f^0 is the tabulated scattering factor and f is that corrected for thermal motion. The isotropic thermal parameters have the form:

$$f = f^0 exp[-B(sin \ \theta/\lambda)^2]$$

where B is related to the mean-square displacement, U^2, of the atom from its mean position by the expression:

$$B = 8\pi^2 U^2$$

PART 1

CRYSTAL AND MOLECULAR STRUCTURE OF

B,B-DIPHENYLBOROXAZOLIDINE (2-AMINOETHYL DIPHENYLBORINATE)

INTRODUCTION

In recent years the boroxazclidines have been extensively studied, the primary concern being the unusual stability of the aminoalcohol esters with respect to boron esters of ordinary alcohols. B,B-diphenylboroxazclidine (1)
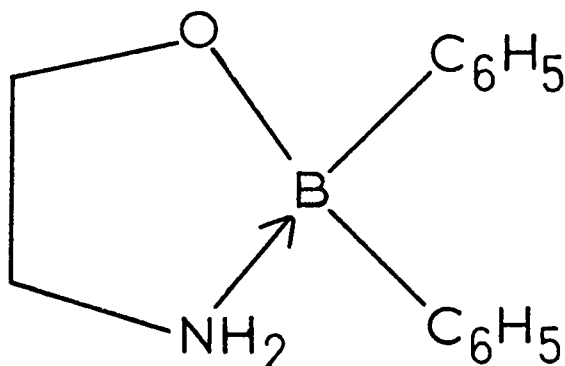
1

was originally prepared by Letsinger and Skoog (7), who correctly proposed the cyclic structure of the ester. The possibility of the N→B dative bond was first proposed by Brown and Fletcher (8) for triethanolamineborate (triptych boroxazolidine) in 1951. The first substantial evidence for the existence of the N→B dative bond in boroxazolidines was the result of detailed kinetic studies of the acid hydrolysis of these compounds by Zimmerman and co-workers, the details of which are the subject of a review article by Zimmerman (9). The X-ray crystallographic study of B,B-diphenylboroxazolidine was undertaken to provide conclusive proof of the existence of the boroxazolidine ring.

EXPERIMENTAL

B,B-Diphenylboroxazolidine was prepared as previously described (7, 10). Recrystallization from 1:1 ethanol-carbon tetrachloride gave colorless needles, elongated along b, with (100), (001), and (101) variously developed. The crystal chosen for study was mounted with b parallel to the goniostat axis and was ca. 0.5 mm in length with a cross section of 0.3 x 0.3 mm. Unit-cell and space group data were obtained from film and diffractometer measurements. The unit-cell parameters were refined by a least-squares treatment of $\sin^2\theta$ values for 22 reflexions measured on a diffractometer with Cu K_α radiation. Crystal data are:
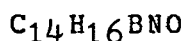
$C_{14}H_{16}BNO$ f.w. = 225.1

Monoclinic, a = 13.840(1), b = 8.9169(5), c = 10.170(1) Å, β = 98.85(1)°, V = 1240.1(2) Å³. Dm = 1.201(5), Z = 4, Dx = 1.2055(3), F(000) = 480 (20° C, Cu K_α, λ = 1.5418 Å, μ = 5.9 cm⁻¹). Absent spectra: 0k0, k ≠ 2n and h0ℓ, h + ℓ ≠ 2n define uniquely the space group $P2_1/n$ (C_{2h}^5, No. 14).

Intensities were measured on a Datex-automated General Electric XRD 6 diffractometer, with a scintillation counter, Cu K_α radiation (nickel filter and pulse height analyser), and a θ-2θ scan at 2° min⁻¹ over a range of (1.80 + 0.86 tan θ) degrees in 2θ, with 20 s background counts being measured at each end of the scan. Data were measured to 2θ = 145° (minimum interplanar spacing 0.81 Å). A check reflexion was monitored every 40 reflexions throughout the data collection.

The intensity of the check reflexion remained within ± 2.5% of its initial value during the data collection, the final value being equal to the initial value. Lorentz and polarization corrections were applied, and the structure amplitudes were derived. No absorption correction was made in view of the low value of μ. Of the 1837 independent reflexions measured, 369 had intensities less than $3\sigma(\underline{I})$ above background where $\sigma^2(\underline{I}) = \underline{S} + \underline{B} + (0.05\underline{S})^2$ with $\underline{S}$ = scan count and $\underline{B}$ = time averaged background count. These reflexions were not included in the refinement.

Structure Analysis

The structure was solved by direct methods. Sixteen sets of signs for 254 reflexions with normalized structure factor $|\underline{E}| \geq 1.50$ were determined by a computer program which uses Sayre relationships in an iterative procedure (11). The starting set of reflexions is given in Table 1. One set of signs was outstanding in that it converged in 5 cycles to a set having the highest consistency index (11) (0.85) with 130 positive signs and 124 negative signs. An $\underline{E}$-map was computed using the 254 signed values of $\underline{E}$ from this set. The 17 non-hydrogen atoms accounted for the 17 highest peaks on the map. A structure factor calculation based on the positions from the $\underline{E}$-map gave $\underline{R}$ 0.211. Two cycles of full-matrix least-squares refinement of the positions and isotropic temperature factors of the boron, nitrogen, oxygen, and carbon atoms reduced $\underline{R}$ to 0.151. All 16 hydrogen atoms were then located from a difference Fourier. One cycle with the non-hydrogen

Table 1

Basic starting set of reflexions for $C_{14}H_{16}BNO$

h	k	ℓ	$|E|$	
6	1	-8	4.00	
3	1	-1	2.25	origin determining
0	2	1	2.20	
6	3	0	3.14	
1	2	-4	2.47	
9	3	-1	3.19	
10	3	4	3.21	

atoms having anisotropic temperature factors and the hydrogen atoms isotropic resulted in $\underline{R}$ = 0.058. Convergence was reached after two more cycles at $\underline{R}$ = 0.041 for 1458 reflexions with $\underline{I} > 3\sigma(\underline{I})$ (10 reflexions were given zero weight in the final stages of refinement due to suspected extinction errors: 0 0 2, 1 0 -1, 2 0 0, 1 1 1, 3 1 -1, 3 2 0, 0 2 0, 0 2 1, 2 2 -1, and 1 3 0).

The scattering factors of ref. 12 were used for the boron, nitrogen, oxygen, and carbon atoms and those of ref. 13 for the hydrogen atoms. The weighting scheme: $\underline{w}$ = 1 if $|\underline{F}o| \leq 10$; $\underline{w}$ = $(10/|\underline{F}o|)^2$ if $|\underline{F}o| > 10$, and $\underline{w}$ = 0.49 for the weak reflexions gave constant average values of $\underline{w}(\underline{F}o - \underline{F}c)^2$ over ranges of $|\underline{F}o|$, and was employed in the final stages of refinement. On the final cycle of refinement, no parameter shift was greater than 0.33 standard deviations. The final positional and thermal parameters are given in Tables 2 and 3 respectively. Measured and calculated structure amplitudes are available on request.

THERMAL MOTION AND CORRECTION OF MOLECULAR GEOMETRY

The thermal motion has been analysed in terms of the rigid-body modes of translation ($\underline{T}$), libration ($\underline{L}$), and screw ($\underline{S}$) motion using the computer program $\underline{MGTLS}$ (14). Four analyses were carried out: the 17 non-hydrogen atoms were considered first, then each of the three rings in the molecule was analysed for rigid-body motion. The analysis of the five-membered ring and attached atoms C(3) and C(9)

Table 2

Final positional parameters (fractional x 10^4)

with estimated standard deviations in parentheses

Atom	x	y	z
B	7785 (2)	2708 (2)	3710 (2)
O	7244 (1)	4803 (1)	3574 (1)
N	7069 (1)	1504 (2)	2904 (2)
C (1)	6243 (2)	3698 (3)	3325 (3)
C (2)	6182 (2)	2385 (3)	2386 (3)
C (3)	8799 (1)	2978 (2)	2988 (2)
C (4)	8782 (2)	2916 (3)	1616 (2)
C (5)	9594 (2)	3304 (3)	1032 (3)
C (6)	10440 (2)	3758 (3)	1796 (3)
C (7)	10487 (2)	3833 (3)	3157 (3)
C (8)	9678 (2)	3449 (2)	3730 (2)
C (9)	8111 (1)	2110 (2)	5216 (2)
C (10)	8600 (2)	759 (3)	5526 (3)
·C (11)	8829 (2)	247 (3)	6827 (3)
C (12)	8591 (2)	1086 (3)	7858 (3)
C (13)	8111 (2)	2418 (4)	7595 (2)
C (14)	7876 (2)	2912 (3)	6289 (2)
H (1)	6010 (18)	3454 (30)	4199 (27)
H (1')	5853 (20)	4484 (32)	2942 (25)
H (2)	6285 (22)	2691 (34)	1518 (31)
H (2')	5598 (19)	1826 (28)	2317 (23)
H (N')	7276 (16)	955 (27)	2321 (24)
H (N)	6900 (20)	776 (34)	3565 (28)
H (4)	8142 (19)	2619 (28)	1026 (25)
H (5)	9514 (19)	3250 (30)	80 (29)
H (6)	11013 (19)	3993 (28)	1398 (25)
H (7)	11087 (21)	4149 (30)	3742 (25)
H (8)	9720 (15)	3520 (26)	4694 (24)
H (10)	8819 (18)	226 (30)	4837 (25)
H (11)	9176 (23)	-700 (38)	6942 (29)
H (12)	8777 (21)	744 (32)	8783 (30)
H (13)	7910 (21)	3063 (35)	8278 (31)
H (14)	7529 (17)	3834 (27)	6127 (21)

Table 3

Final thermal parameters and

their estimated standard deviations

(a) Anisotropic thermal parameters ($\underline{U}_{11}$ x 100 $\overset{\circ}{A}{}^2$)

Atom	$\underline{U}_{11}$	$\underline{U}_{22}$	$\underline{U}_{33}$	$\underline{U}_{12}$	$\underline{U}_{13}$	$\underline{U}_{23}$
B	5.2 (1)	4.0 (1)	5.7 (1)	-0.1 (1)	1.1 (1)	-0.6 (1)
O	3.9 (1)	3.3 (1)	5.6 (1)	0.1 (1)	0.9 (1)	0.1 (1)
N	4.9 (1)	3.9 (1)	5.6 (1)	-0.4 (1)	1.1 (1)	-0.8 (1)
C (1)	4.3 (1)	4.8 (1)	8.3 (2)	0.2 (1)	0.8 (1)	0.1 (1)
C (2)	4.8 (2)	5.9 (2)	7.8 (2)	-0.8 (1)	-0.5 (1)	-0.4 (1)
C (3)	4.3 (1)	3.1 (1)	4.5 (1)	0.3 (1)	0.8 (1)	0.0 (1)
C (4)	5.3 (1)	5.4 (1)	4.8 (1)	-0.1 (1)	1.2 (1)	-0.2 (1)
C (5)	7.3 (2)	6.5 (2)	5.2 (2)	0.1 (1)	2.5 (1)	0.2 (1)
C (6)	5.7 (2)	5.6 (2)	8.0 (2)	0.3 (1)	3.2 (1)	1.2 (1)
C (7)	4.4 (1)	5.7 (2)	7.7 (2)	-0.4 (1)	1.1 (1)	0.4 (1)
C (8)	4.7 (1)	5.0 (1)	5.0 (1)	-0.2 (1)	0.9 (1)	-0.1 (1)
C (9)	4.0 (1)	3.6 (1)	4.9 (1)	-0.5 (1)	1.0 (1)	0.1 (1)
C (10)	7.3 (2)	4.0 (1)	6.3 (2)	0.4 (1)	0.8 (1)	0.3 (1)
C (11)	7.9 (2)	4.7 (2)	8.1 (2)	-0.4 (1)	-0.8 (2)	2.1 (1)
C (12)	6.7 (2)	8.1 (2)	5.5 (2)	-2.5 (2)	-0.1 (1)	1.8 (2)
C (13)	6.0 (2)	8.7 (2)	4.7 (1)	-0.9 (1)	1.3 (1)	-0.1 (1)
C (14)	4.8 (1)	5.5 (2)	5.1 (1)	0.1 (1)	1.2 (1)	-0.1 (1)

(b) Isotropic thermal parameters

Atom	$\underline{B}(\overset{\circ}{A}{}^2)$	Atom	$\underline{B}(\overset{\circ}{A}{}^2)$
H (1)	5.9 (6)	H (6)	5.9 (6)
H (1')	5.7 (6)	H (7)	6.0 (6)
H (2)	7.1 (8)	H (8)	4.6 (5)
H (2')	5.0 (5)	H (10)	5.4 (6)
H (N)	6.8 (7)	H (11)	7.5 (7)
H (N')	4.1 (5)	H (12)	6.9 (7)
H (4)	5.8 (6)	H (13)	7.7 (8)
H (5)	6.2 (6)	H (14)	4.2 (5)

failed to give a positive-definite $\underline{L}$ tensor. The r.m.s. $\Delta \underline{U}_{ij}$ of 0.0055 Å² for the molecule as a whole is significantly larger than the r.m.s. standard deviation in the thermal parameters $\underline{U}_{ij}$ (0.0013 Å²), indicating that the molecule as a whole is not a good rigid-body. The analyses of the two phenyl groups were successful and the results appear in Table 4.

The r.m.s. $\Delta \underline{U}_{ij}$ values of 0.0019 and 0.0023 Å² for the phenyl groups indicate that the thermal motion of the groups is adequately described by the rigid-body parameters in Table 4. Both groups show nearly isotropic translational motion and anisotropic librational motion. The orientation of the principal axes of $\underline{L}$ is as expected: the largest oscillations, $\underline{L}_1$, correspond to rotations about the B-C bonds, the angles between the $\underline{L}_1$ axes and the bonds being 7.7 (C(3)) and 14.5° (C(9)).

The appropriate bond distances and angles in the phenyl groups have been corrected for libration (15,16) using shape parameters $\underline{q}^2$ of 0.08 for all atoms. Corrected bond distances appear in Table 5 and both corrected and uncorrected bond angles in Table 6.

RESULTS AND DISCUSSION

The X-ray analysis confirms the cyclic structure first proposed for this compound by Letsinger and Skoog (7). Figure 1 shows the molecule viewed down the $\underline{b}$ axis. Individual bond lengths (not corrected for libration) with their standard

Table 4

Rigid-body thermal parameters[1]

	C(3)-C(8), B			C(9)-C(14), B		
$\underline{L}$ (deg²)	⌈ 38(6)	6(3)	-12(3) ⌉	⌈ 18(2)	2(2)	14(4) ⌉
	|	20(2)	-3(2) |	|	17(3)	-12(4) |
	⌊		15(3) ⌋	⌊		47(8) ⌋

Principal axes of $\underline{L}$

r.m.s. Amplitude		Direction cosines (x10³)					
6.7°	-882	-273	385	7.5°	-321	274	-907
4.2	-269	961	65	4.4	-685	-728	23
3.2	-388	-46	-921	2.7	-654	628	421

Principal axes of reduced $\underline{T}$

r.m.s. Amplitude		Direction cosines (x10³)					
0.21 Å	522	12	853	0.22 Å	-230	126	-965
0.21	832	215	-511	0.19	-851	445	262
0.18	-189	977	102	0.18	463	887	5

Displacement of axes from intersecting (Å)

Parallel to $\underline{L}$(1)	0.09	0.69
Parallel to $\underline{L}$(2)	-0.01	0.29
Parallel to $\underline{L}$(3)	0.11	-0.03

Effective screw translations (Å)

Parallel to $\underline{L}$(1)	-0.003	0.014
Parallel to $\underline{L}$(2)	-0.017	-0.025
Parallel to $\underline{L}$(3)	0.028	0.003

Fractional coordinates of unique origin (x10⁴)

$\underline{x}$	8830	8156
$\underline{y}$	3087	2595
$\underline{z}$	3030	5136

Fractional coordinates of centre of gravity (x10⁴)

$\underline{x}$	9398	8288
$\underline{y}$	3286	1734
$\underline{z}$	2559	6181

r.m.s. $\Delta \underline{U}_{11}$	0.0019	0.0023 Å²

[1]Axes of reference are orthogonal angstrom axes. E.s.d.'s of components of $\underline{L}$ are given in parentheses in units of the last places shown.
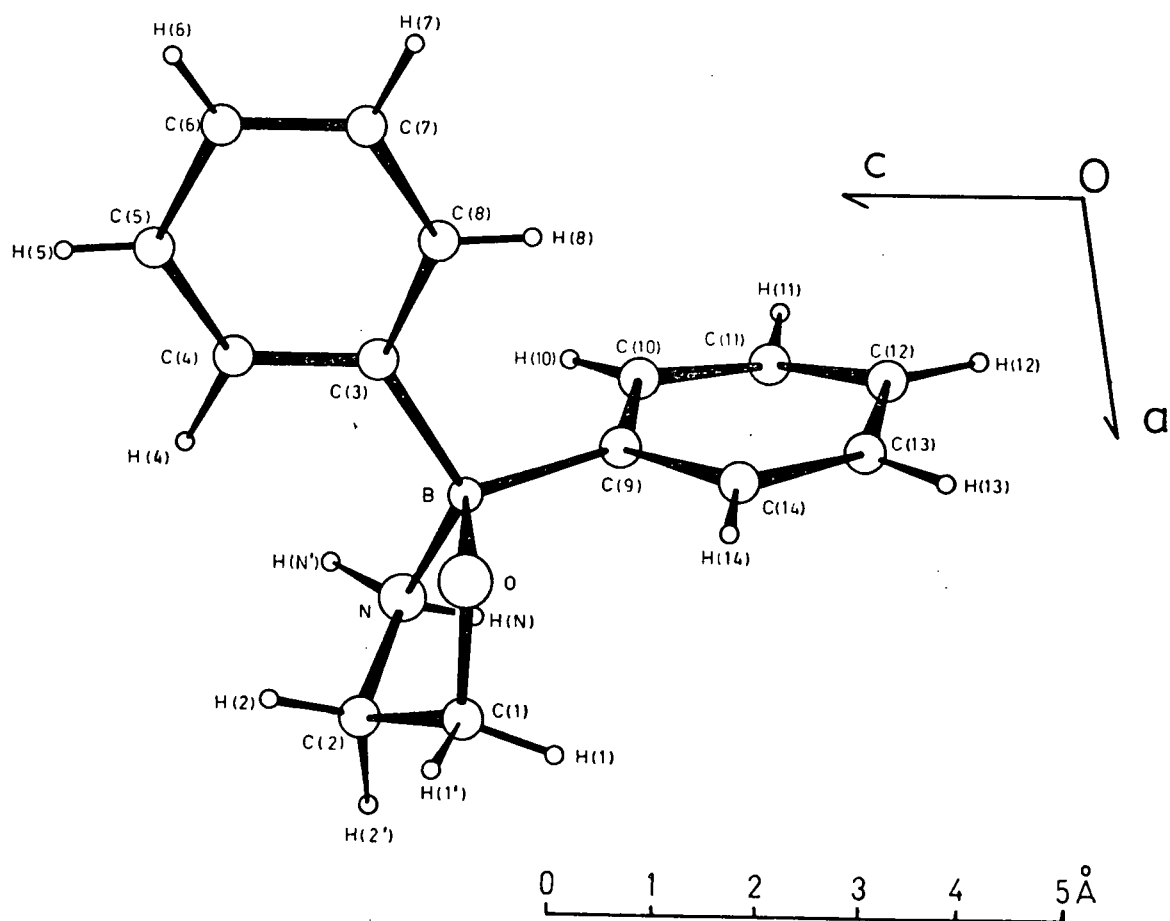
Figure 1

The molecule viewed down <u>b</u>, showing crystallographic numbering scheme.
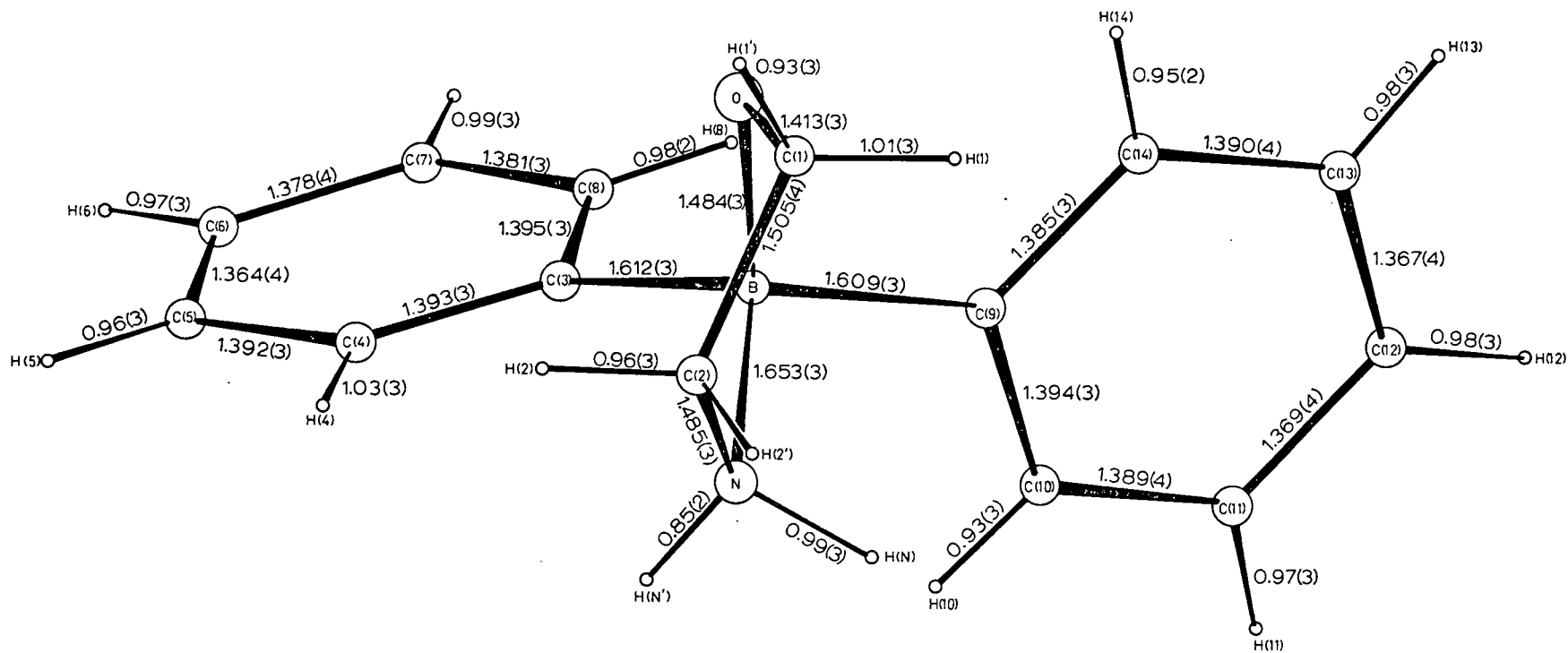
Figure 2

A general view of the molecule with bond distances (Å) and their standard deviations in parentheses. The C(2)-H(2') distance is 0.94(3) Å.

deviations are shown in Figure 2 and mean bond lengths are given in Table 5.

The five-membered boroxazolidine ring is approximately in the half-chair conformation, with C(2) displaced 0.08 Å from the BON plane and C(1) lying 0.50 Å on the opposite side of the BON plane. The dihedral angles in the ring (see Table 7) are in good agreement with those obtained from minimum energy calculations for w_1 = 25° (17), also shown in Table 7. The observed magnitudes of the dihedral angles are slightly smaller than the calculated values since the mean valence angle in the ring, 104.8°, is slightly greater than the calculated value of 104.2°. Angles in the five-membered ring range from 99.7(1) at B to 110.1(2)° at O. The angular strain in the ring is partially relieved by a shortening of the C(1)-C(2) bond to 1.505 Å from the expected value of 1.537 Å (18) for a C(sp^3)-C(sp^3) bond and a lengthening of the B-N bond to 1.653 Å from the mean value of 1.55 Å (18) for B(sp^3)-N(sp^3) bonds. The isoelectronic N-C (1.485 Å) and O-B (1.484 Å) bonds as well as the C-O bond (1.413 Å) are normal single bonds (18).

The two phenyl groups are planar within experimental error (see Table 8). All of the phenyl hydrogen atoms lie in the respective phenyl planes with the exception of H(10) which lies 0.08 Å (3 standard deviations) below the C(9)-C(14) plane. The boron atom deviates significantly from both phenyl planes, being displaced 0.15 from the C(3)-C(8) plane and -0.02 Å from the C(9)-C(14) plane representing a slight

Table 5

(a) Mean bond lengths (Å), with
r.m.s. deviations in parentheses*

Atoms	number of values	uncorrected	corrected
B-C	2	1.611(2)	1.616(2)
B-N	1	1.653(3)	
B-O	1	1.484(3)	
C-C	1	1.505(4)	
C-C(ar)	12	1.383(11)	1.392(11)
C-N	1	1.485(3)	
C-O	1	1.413(3)	
C-H	4	0.96(3)	
C-H(ar)	10	0.974(25)	
N-H	2	0.92(7)	

(b) Bond lengths corrected for libration

Atoms	distance	Atoms	distance
B-C(3)	1.617	B-C(9)	1.614
C(3)-C(4)	1.404	C(9)-C(10)	1.405
C(4)-C(5)	1.398	C(10)-C(11)	1.395
C(5)-C(6)	1.373	C(11)-C(12)	1.381
C(6)-C(7)	1.388	C(12)-C(13)	1.377
C(7)-C(8)	1.386	C(13)-C(14)	1.395
C(8)-C(3)	1.404	C(14)-C(9)	1.397

*For single value parameters, the least-squares standard deviation is given in parentheses.

Table 6

Bond angles (deg) with estimated

standard deviations in parentheses

(a) Non-hydrogen atoms

Atoms	uncorr.	corr.
O-B-C(3)	108.9(2)	-----
O-B-C(9)	113.7(2)	-----
O-B-N	99.7(1)	-----
C(3)-B-C(9)	114.0(2)	-----
C(3)-B-N	112.9(2)	-----
C(9)-B-N	106.8(2)	-----
B-O-C(1)	110.1(2)	-----
C(2)-N-B	106.1(2)	-----
O-C(1)-C(2)	105.2(2)	-----
N-C(2)-C(1)	102.9(2)	-----
B-C(3)-C(4)	124.1(2)	124.0
B-C(3)-C(8)	120.0(2)	119.9
C(8)-C(3)-C(4)	115.6(2)	115.8
C(3)-C(4)-C(4)	121.8(2)	121.7
C(4)-C(5)-C(6)	120.6(2)	120.5
C(5)-C(6)-C(7)	119.3(2)	119.6
C(6)-C(7)-C(8)	119.7(2)	119.6
C(7)-C(8)-C(3)	122.9(2)	122.8
B-C(9)-C(10)	122.0(2)	121.8
B-C(9)-C(14)	122.4(2)	122.3
C(10)-C(9)-C(14)	115.6(2)	115.9
C(9)-C(10)-C(11)	122.1(3)	121.9
C(10)-C(11)-C(12)	120.2(3)	120.1
C(11)-C(12)-C(13)	119.5(3)	119.7
C(12)-C(13)-C(14)	119.8(3)	119.7
C(13)-C(14)-C(9)	122.8(2)	122.7

(b) Angles involving hydrogen atoms

Atoms	value	Atoms	value
H(N)-N-H(N')	104(2)	H(5)-C(5)-C(4)	116(2)
H(N)-N-B	107(2)	H(5)-C(5)-C(6)	123(2)
H(N)-N-C(2)	109(2)	H(6)-C(6)-C(5)	121(2)
H(N')-N-C(2)	114(2)	H(6)-C(6)-C(7)	120(2)
H(N')-N-B	117(2)	H(7)-C(7)-C(6)	122(2)
H(1)-C(1)-H(1')	107(2)	H(7)-C(7)-C(8)	119(2)
H(1)-C(1)-O	109(1)	H(8)-C(8)-C(3)	118(1)
H(1)-C(1)-C(2)	113(2)	H(8)-C(8)-C(7)	119(1)
H(1')-C(1)-O	112(2)	H(10)-C(10)-C(9)	118(2)
H(1')-C(1)-C(2)	110(2)	H(10)-C(10)-C(11)	120(2)
H(2)-C(2)-H(2')	109(2)	H(11)-C(11)-C(10)	116(2)
H(2)-C(2)-N	104(2)	H(11)-C(11)-C(12)	124(2)
H(2)-C(2)-C(1)	111(2)	H(12)-C(12)-C(11)	120(2)
H(2')-C(2)-N	114(2)	H(12)-C(12)-C(13)	120(2)
H(2')-C(2)-C(1)	115(2)	H(13)-C(13)-C(12)	124(2)
H(4)-C(4)-C(3)	118(1)	H(13)-C(13)-C(14)	116(2)
H(4)-C(4)-C(5)	120(1)	H(14)-C(14)-C(13)	118(1)
		H(14)-C(14)-C(9)	119(1)

Table 7

Intra-annular torsion angles (deg)

Boroxazolidine ring

Bond	observed	calc.
B-C	-22.0(2)	-25.0
O-C(1)	39.6(2)	41.6
C(1)-C(2)	-39.3(2)	-42.3
C(2)-N	24.8(2)	25.9
N-B	-3.1(2)	-1.3

Table 8

Weighted least-squares mean planes

(a) Distances (Å) of relevant atoms from the mean planes

Atom	d	d/σ	Atom	d	d/σ
Plane 1: C(3)-C(8)			**Plane 2: C(9)-C(14)**		
C(3)	0.000	0.0	C(9)	-0.001	0.4
C(4)	-0.001	0.4	C(10)	-0.003	1.2
C(5)	0.001	0.5	C(11)	0.007	2.4
C(6)	0.000	0.1	C(12)	-0.004	1.4
C(7)	-0.001	0.3	C(13)	-0.001	0.5
C(8)	0.001	0.3	C(14)	0.003	1.3
B	0.150	67.4	B	-0.025	10.7
H(4)	0.040	1.6	H(10)	-0.080	3.1
H(5)	0.020	0.7	H(11)	-0.007	0.2
H(6)	-0.032	1.3	H(12)	-0.035	1.2
H(7)	-0.007	0.3	H(13)	0.006	0.2
H(8)	0.012	0.5	H(14)	0.023	1.0

(b) Equations of planes: $\ell X + mY + nZ = p$, where X, Y, and Z are orthogonal angstrom coordinates derived as follows:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a & 0 & c\cos \\ 0 & b & 0 \\ 0 & 0 & c\sin \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$$

Plane	ℓ	m	n	p
(1)	-0.3074	0.9482	-0.0800	-1.3230
(2)	-0.8579	-0.4573	-0.0823	-10.4443

The dihedral angle between plane normals is 100°

folding of the two planes away from each other. The angle between phenyl plane normals is 100°. The two rings are not equivalent as the C(3)-C(8) ring is twisted 21° with respect to the BNC(3) plane while the C(9)-C(14) ring lies nearly in the BOC(9) plane, dihedral angle 7°. The C-C(ar) distances range from 1.373 to 1.405 Å with a mean value of 1.392(11) Å, in good agreement with the accepted mean of 1.394 Å (18). There are, however, significant differences between the individual C-C distances in the phenyl rings. There is a noticeable trend toward shortening of the C-C distances as they are removed from the boron substituent. This is due to a combination of steric and electronic effects which are discussed in more detail in Part 2. The boron-carbon distances, mean 1.616(2), are significantly shorter than the B-C distances of 1.631(9)-1.646(8) Å found in the tetraphenyl borate anion (19), in accord with electron delocalization.

The mean bond angles at tetrahedrally and trigonally coordinated atoms are 109.4 and 120.0° respectively. There are a number of significant deviations from these values, resulting from steric and charge delocalization effects. Intramolecular contacts between atom pairs N and C(4), N and C(10), and O and C(14) are responsible for angular distortions at the boron atom, and at carbon atoms C(3) and C(9). Expansion of the angles NBC(3), OBC(9), BC(3)C(4), BC(9)C(14), and BC(9)C(10) [112.9, 113.7, 124.0, 122.3, and 121.8° respectively] allows the distances C(4)...N (3.143), O...C(14) (2.955), and N...C(10) (3.210 Å) to be equal to or slightly greater than the sum of van der Waals radii. The

expansion of OBC(9) and NBC(3) causes a contraction of NBC(9) to 106.8° which is balanced by an expansion of BC(9)C(10) (as above) to allow the N...C(10) contact to be normal. The phenyl C-C-C angles at C(3) and C(9) are both contracted to a mean value of 115.9° as a result of expansion of the B-C-C angles. This, in turn, makes angular adjustments at the remaining phenyl carbon atoms necessary to retain the planarity of the phenyl rings. The magnitude of these distortions is also dependent on the electron delocalization in as much as the C-C distances are not all equal.

The angle opposite the small OBN angle (99.7°) is opened to 114.0° and is normal for the angle between two bulky substituents. The interior angles in the boroxazolidine ring, as previously mentioned, are all contracted as are the H-N-H and H-C-H angles opposite them, all of which are less than, but not significantly different from the tetrahedral angle. The remaining angles involving the ring hydrogen atoms are generally greater than the tetrahedral angle. The angles H(N')-N-C(2) (113.9°) and H(N')-N-B (116.9°) represent bending of H(N') toward the oxygen atom to which it is hydrogen bonded. Bond angles involving phenyl hydrogen atoms show a trend that when adjacent C-C distances are different, so are the corresponding H-C-C angles. The H-C-C angle which involves the carbon atom nearer the vertex atom is larger than the other H-C-C angle. As the difference between adjacent C-C distances increases, so does that between the H-C-C angles. An example is C(11), where C(10)-C(11) (1.395) is five standard deviations longer than C(11)-C(12) (1.381 Å)
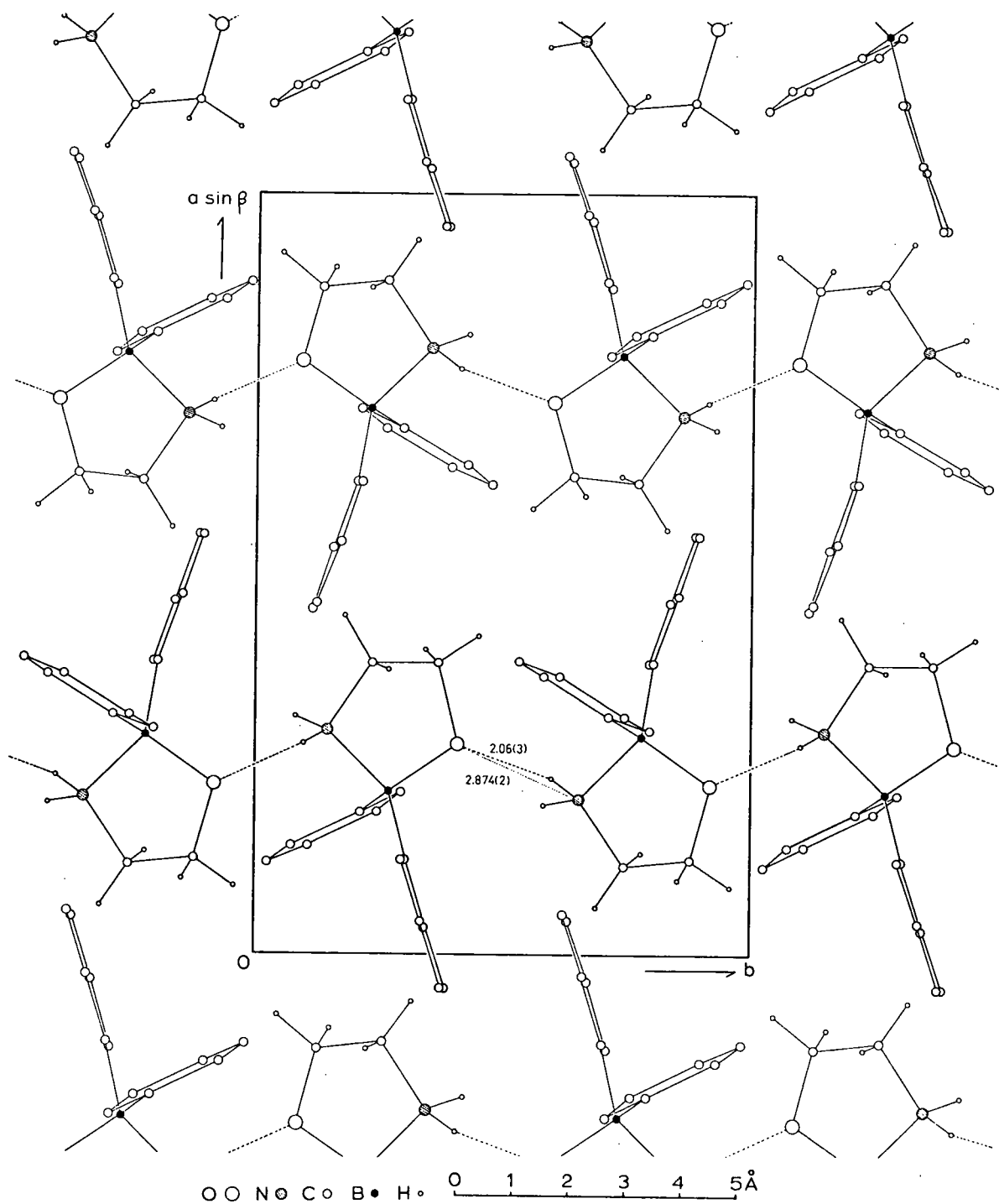
Figure 3

The structure viewed down c; hydrogen bonds are represented by broken lines.

Table 9

(a) Selected intra- and intermolecular contacts

Intramolecular		Intermolecular*	
Atoms	distance	Atoms	distance
O...C(14)	2.955(3)	N...C(3)[1]	3.437(3)
O...C(8)	3.395(3)	N...C(4)[1]	3.470(3)
O...C(4)	3.299(2)	C(4)...H(N)[2]	2.72(3)
N...C(4)	3.143(3)	C(7)...H(11)[3]	2.84(3)
N...C(10)	3.201(3)	C(11)...H(1')[4]	2.87(3)
		C(12)...H(14)[5]	2.83(2)
		C(14)...H(7)[6]	2.99(3)

(b) Hydrogen-bond data (distances in Å and angles in deg)

D-H...A	H...A	D...A	∠DHA	∠XAH
N-H(N')...O[7]	2.06(3)	2.874(2)	160(2)	119.5(6),119.6(6)

*Superscripts refer to atoms at positions:

[1]	3/2-x	y-1/2	1/2-z	[5]	3/2-x	y-1/2	3/2-z
[2]	3/2-x	1/2+y	1/2-z	[6]	2-x	1-y	1-z
[3]	2-x	-y	1-z	[7]	3/2-x	y-1/2	1/2+z
[4]	1/2+x	1/2-y	1/2+z			

and the angles H-C(11)-C(10) (115.9) and H-C(11)-C(12) (123.8°) differ by more than four standard deviations.

The mean C-H, C-H(ar), and N-H bond lengths of 0.96(3), 0.97(3), and 0.92(7) Å are as expected. The distances are shorter than those obtained spectroscopically indicating that the hydrogen electron has been pulled toward the atom to which it is bonded.

Figure 3 shows the structure viewed down c. The crystal structure consists of discrete molecules of B,B-diphenylboroxazolidine which are linked by O...H-N hydrogen bonds (O...N = 2.874 Å) to form continuous spirals about the 2₁ axes along b. Details of the hydrogen bonding scheme are given in Table 9 as well as inter- and intramolecular contacts less than 3.5 Å. There are only two heavy atom intermolecular contacts less than 3.5 Å: N...C(3), 3.437, and N-C(4), 3.470 Å (apart from the hydrogen bond). These, and all other intermolecular contacts correspond to van der Waals interactions.

PART 2

CRYSTAL AND MOLECULAR STRUCTURE OF

B,B-BIS(p -FLUOROPHENYL)BOROXAZOLIDINE

INTRODUCTION

The cyclic structure of B,B-diphenylboroxazolidine (1, Part 1) has been established as has that of triethanolamine borate (TEAB) (20), confirming the existence of the N→B dative bond in these esters. The X-ray analysis of B,B-bis(p-fluorophenyl)boroxazolidine (2) was undertaken to study the structural effects of the fluorine substituent both in the phenyl rings and in the five-membered ring. The density of 2 and crystallization in a different space group than 1 suggested the possibility of an F...H-N hydrogen bond for which there are only limited structural data, particularly for organic structures.
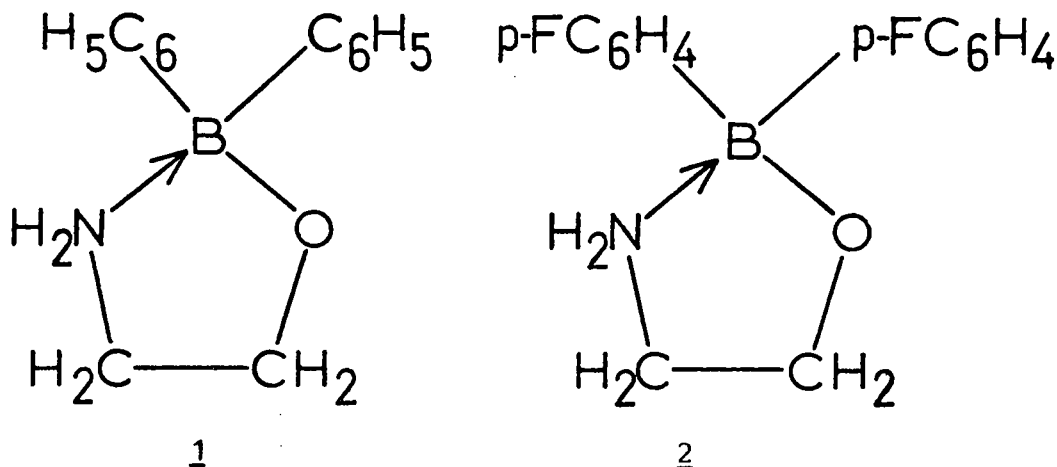
EXPERIMENTAL

Recrystallization of B,B-bis(p-fluorophenyl)boroxazolidine from ethanol gave colorless, regular crystals elongated along b. The specimen used for data collection was bounded by the (011) and (101) planes, at distances of 0.27 and 0.13 mm

respectively from an internal origin and was mounted with $\underline{b}$ parallel to the goniostat axis. Unit-cell and space group data were obtained from film and diffractometer measurements. The unit-cell parameters were refined by a least-squares treatment of $\sin^2\theta$ values for 30 reflexions measured on a diffractometer with Cu K_α radiation. Crystal data are:

$C_{14}H_{14}BF_2NO$ f.w. = 261.1

Orthorhombic, $\underline{a}$ = 13.442(4), $\underline{b}$ = 10.214(3), $\underline{c}$ = 9.283(2) Å, $\underline{V}$ = 1274.5(6) Å^3, $\underline{Dm}$ = 1.37 (flotation in aqueous KI) , $\underline{Z}$ = 4, $\underline{Dx}$ = 1.361 g cm^{-3}, $\underline{F}$(000) = 544 (20°C, Cu K_α, λ = 1.5418 Å, μ = 9.0 cm^{-1}). Absent reflexions: $\underline{h}$00, $\underline{h} \neq 2\underline{n}$, 0$\underline{k}$0, $\underline{k} \neq 2\underline{n}$, and 00$\underline{l}$, $\underline{l} \neq 2\underline{n}$ define uniquely the space group $\underline{P}2_1 2_1 2_1$ ($\underline{D}_2^4$, No. 19).

Intensities were measured on a Datex-automated General Electric XRD 6 diffractometer, with a scintillation counter, Cu K_α radiation (nickel filter and pulse height analyser), and a θ-2θ scan at 2° min^{-1} over a range of (1.80 + 0.86 tan θ) degrees in 2θ, with 20 s background counts being measured at each end of the scan. Data were measured to 2θ = 145° (minimum interplanar spacing 0.81 Å). The r.m.s. deviation of the intensity of the check reflexion, measured every 40 reflexions throughout the data collection, from its initial value was 1.4%. The final intensity was 99% of the initial value. Lorentz, polarization, and absorption corrections were applied, and the structure amplitudes were derived. Of 1481 independent reflexions measured, 231 had intensities less than $3\sigma(\underline{I})$ above background where $\sigma^2(\underline{I})$ = $\underline{S}$ + $\underline{B}$ + $(0.03\underline{S})^2$

with $\underline{S}$ = scan count and $\underline{B}$ = background count, corrected to time of scan. These reflexions were not included in the refinement.

Structure Analysis

The structure was solved by direct methods, 200 reflexions with normalized structure factor $|\underline{E}| \geq 1.45$ being used in the symbolic addition procedure for non-centrosymmetric crystals (21). The phases of the 11 1 0, 2 0 5, and 6 7 0 reflexions were fixed to define the origin and that of 1 0 3 was fixed at +250mc to specify the enantiomorph. During a manual expansion, carried out among the 70 reflexions with largest $|\underline{E}|$ values, symbol phases were assigned to the 0 5 1, 10 10 1, and 13 3 6 reflexions. The phase of 0 5 1 must be ±250 mc and manual indications gave two possible values for each of the other symbols, near ±250 mc for both 10 10 1 and 13 3 6. These seven reflexions comprise the basic starting group given in Table 10.

Eight starting sets were generated by allowing each of the three symbol phases to have initial values of ±250 mc. These sets were used as input to a computer program which determines phases using the tangent formula (22,23). The values of overall $\underline{t}$ overall $\propto$, $\underline{Q}$, and $\underline{Rk}$ on the final cycle for each of the sets are given in Table 11. Set 1, which had the lowest value of $\underline{Rk}$, was expanded to 228 reflexions with $|\underline{E}| \geq 1.40$ by using as starting values for the symbols $\underline{a}$, $\underline{b}$, and $\underline{c}$ those calculated in set 1, +250, +277, and +135 mc

Table 10

Basic starting set of reflexions for $C_{14}H_{14}BF_2NO$

$\underline{h}$	$\underline{k}$	$\underline{\ell}$	$|\underline{E}|$	phase (mc)	
11	1	0	4.58	250	
2	0	5	3.71	250	origin determining
6	7	0	3.51	0	
1	0	3	2.43	250	enantiomorph
0	5	1	2.21	$\underline{a}$	
10	10	1	2.27	$\underline{b}$	
13	3	6	2.26	$\underline{c}$	

Table 11

Results for the eight starting sets

in the phase determination procedure

Set	$\underline{a}$(mc)	$\underline{b}$(mc)	$\underline{c}$(mc)	$\underline{t}$	$\propto$	$\underline{Q}$	$\underline{Rk}$	$\underline{N}$
1	250	250	250	0.59	180	0.39	0.20	193
2	250	250	-250	0.54	129	0.44	0.35	178
3	250	-250	250	0.58	156	0.40	0.35	178
4	250	-250	-250	0.55	155	0.43	0.33	177
5	-250	250	250	0.53	122	0.46	0.38	172
6	-250	250	-250	0.54	141	0.45	0.33	173
7	-250	-250	250	0.55	138	0.44	0.35	176
8	-250	-250	-250	0.57	155	0.41	0.33	173

respectively. A new symbol, 10 6 0, was allowed to take either of its two possible values, 0 or 500 mc. The two resulting values of $\underline{Rk}$ were 0.17 with 10 6 0 having a phase of 500 mc and 0.36 with 10 6 0 at 0 mc. An $\underline{E}$ -map based on the set of 214 determined phases with $\underline{Rk}$ = 0.17 clearly gave the structure, the 19 highest peaks corresponding to the 19 non-hydrogen atoms.

Two cycles of full-matrix least-squares refinement of the positional and isotropic thermal parameters of the non-hydrogen atoms gave $\underline{R}$ 0.121. This was followed by two cycles of anisotropic refinement which reduced $\underline{R}$ to 0.093. A difference map at this point revealed the positions of all 14 hydrogen atoms which were included in all subsequent refinement with isotropic thermal parameters. Convergence was reached after two more cycles with $\underline{R}$ = 0.047 for 1234 reflexions with $\underline{I} > 3\sigma(\underline{I})$ (16 reflexions were given zero weight in the final stages of refinement due to suspected extinction errors). The mirror image ($\underline{y}$ to $-\underline{y}$) was also refined to convergence giving an $\underline{R}$ value of 0.047. Application of Hamilton's test (24) did not show a significant difference between the $\underline{R}$ factors for the two enantiomorphs.

The scattering factors for the F, O, N, C, and B atoms were taken from ref. 12 and those for hydrogen from ref. 13. The values used for anomalous dispersion corrections $\Delta\underline{f}'$ and $\Delta\underline{f}''$ were as follows: 0.068 and 0.056 for F, 0.050 and 0.032 for O, 0.034 and 0.019 for N, and 0.020 and 0.010 for C. The

values for C and O are those of Hope, de la Camp, and Thiessen (25). The weighting scheme: w = 1 if $|F_o| \leq 7$; w = $(7/|F_o|)^2$ if $|F_o| > 7$; and w = 0.2025 for the weak reflexions gave constant average values of $w(F_o - F_c)^2$ over ranges of $|F_o|$, and was employed in the final stages of refinement. On the final cycle of refinement, no parameter shift was greater than 0.19 standard deviations. Final positional and thermal parameters appear in tables 12 and 13 respectively. Observed and calculated structure amplitudes are available on request.

THERMAL MOTION AND CORRECTION OF MOLECULAR GEOMETRY

The ellipsoids of thermal motion for the non-hydrogen atoms are shown in figure 4. The thermal motion has been analysed in terms of the rigid-body modes as previously described. Four analyses were carried out: the 19 non-hydrogen atoms were considered first and indications of significant independent motion in the phenyl rings prompted separate analyses of the fluorophenyl groups along with the boron atom; finally an analysis of the five-membered ring and atoms C(3) and C(9) failed to give a positive-definite $\underline{L}$ tensor (as for the parent molecule $\underline{B}$,$\underline{B}$-diphenylboroxazolidine in Part 1). The results of the analyses for the two fluorophenyl groups are compiled in table 14.

The r.m.s. standard deviation in the temperature factors $\underline{U}_{ij}$ is 0.0016 $\mathring{A}^2$ which indicates that the entire molecule (r.m.s. $\Delta \underline{U}_{ij}$ = 0.0063 $\mathring{A}^2$) is not a good rigid-body (this was

Table 12

Final positional parameters (fractional x 10^4)

with estimated standard deviations in parentheses

Atom	x	y	z
F(1)	11462 (2)	6938 (2)	3863 (3)
F(2)	8699 (2)	-1240 (2)	7146 (3)
O	7244 (1)	4697 (2)	59011 (2)
N	7190 (2)	3839 (3)	3503 (3)
C(1)	6247 (3)	4345 (4)	5584 (4)
C(2)	6182 (3)	4267 (5)	3979 (5)
C(3)	8903 (2)	4762 (3)	4603 (3)
C(4)	9786 (2)	4182 (3)	4154 (4)
C(5)	10644 (2)	4892 (4)	3886 (4)
C(6)	10613 (2)	6221 (3)	4063 (3)
C(7)	9770 (3)	6852 (3)	4498 (5)
C(8)	8921 (2)	6120 (3)	4749 (4)
C(9)	8102 (2)	2467 (3)	5523 (3)
C(10)	8091 (3)	2218 (3)	7007 (4)
C(11)	8297 (3)	984 (4)	7550 (4)
C(12)	8501 (2)	-17 (3)	6622 (4)
C(13)	8502 (3)	157 (4)	5167 (4)
C(14)	8301 (3)	1411 (3)	4648 (4)
B	7903 (2)	3942 (3)	4949 (3)
H(N1)	7142 (27)	3036 (38)	3166 (41)
H(N2)	7413 (30)	4315 (38)	2642 (50)
H(1A)	5361 (34)	5032 (47)	5882 (50)
H(1B)	6082 (29)	3462 (44)	5906 (43)
H(2A)	5673 (43)	3722 (56)	3625 (65)
H(2B)	6132 (30)	5143 (44)	3539 (47)
H(4)	9773 (28)	3228 (38)	3943 (41)
H(5)	11246 (38)	4516 (51)	3733 (55)
H(7)	9769 (38)	7868 (51)	4574 (52)
H(8)	8361 (27)	6565 (36)	5040 (42)
H(10)	7962 (33)	2925 (40)	7618 (48)
H(11)	8219 (46)	736 (58)	8513 (71)
H(13)	8656 (38)	-615 (52)	4683 (53)
H(14)	8267 (30)	1454 (40)	3569 (47)

Table 13

Final thermal parameters and

their estimated standard deviations

(a) Anisotropic thermal parameters (U_{ij} x 100 $\overset{\circ}{A}{}^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
F(1)	4.8(1)	7.7(2)	7.0(1)	-2.0(1)	0.8(1)	-0.1(1)
F(2)	8.7(2)	4.9(1)	9.6(2)	0.3(1)	-1.1(2)	3.0(1)
O	4.1(1)	4.3(1)	5.0(1)	-0.1(1)	0.6(1)	-1.0(1)
N	4.6(1)	3.4(1)	4.2(1)	-0.0(1)	-0.4(1)	0.4(1)
C(1)	4.0(2)	5.9(2)	6.8(2)	-0.2(2)	0.8(2)	-1.1(2)
C(2)	3.7(2)	7.8(3)	6.4(2)	0.1(2)	-0.4(2)	0.3(2)
C(3)	3.7(1)	3.8(1)	3.7(1)	0.2(1)	0.1(1)	-0.0(1)
C(4)	4.2(2)	4.3(2)	5.9(2)	0.5(1)	0.1(1)	-0.6(2)
C(5)	3.6(2)	6.0(2)	5.8(2)	0.6(2)	0.5(2)	-0.4(2)
C(6)	4.1(2)	5.4(2)	4.2(2)	-0.8(1)	0.3(1)	0.2(2)
C(7)	5.6(2)	3.6(2)	7.7(2)	-0.3(1)	0.9(2)	0.4(2)
C(8)	4.3(2)	4.2(2)	6.1(2)	0.3(1)	0.7(2)	-0.0(2)
C(9)	3.6(1)	3.8(1)	4.0(2)	-0.4(1)	0.1(1)	0.4(1)
C(10)	7.8(2)	4.7(2)	3.3(2)	-1.3(2)	-0.8(2)	0.2(1)
C(11)	8.2(3)	6.3(2)	4.3(2)	-1.4(2)	-1.5(2)	1.8(2)
C(12)	4.3(2)	4.1(2)	6.8(2)	-0.3(1)	-1.0(2)	1.9(2)
C(13)	5.9(2)	4.5(2)	6.3(2)	1.4(2)	0.4(2)	0.3(2)
C(14)	6.6(2)	4.8(2)	4.4(2)	1.2(2)	0.6(2)	0.4(1)
B	3.8(2)	3.8(2)	3.6(1)	-0.1(1)	0.2(1)	-0.3(1)

(b) Isotropic thermal parameters

Atom	$B(\overset{\circ}{A}{}^2)$	Atom	$B(\overset{\circ}{A}{}^2)$
H(N1)	3.5(7)	H(5)	6.1(11)
H(N2)	4.8(9)	H(7)	6.6(12)
H(1A)	5.1(10)	H(8)	3.4(7)
H(1B)	4.1(8)	H(10)	5.2(9)
H(2A)	7.2(13)	H(11)	8.6(15)
H(2B)	4.7(9)	H(13)	5.9(11)
H(4)	3.9(7)	H(14)	4.9(9)

Table 14

Rigid-body thermal parameters[1]

	F(1), C(3)-C(8), B			F(2), C(9)-C(14), B		
$\underline{L}$ (deg^2)	⌈ 53(6)	22(3)	-11(3) ⌉	⌈ 14(3)	-14(6)	4(3) ⌉
	|	17(4)	-3(2) |	|	78(10)	-20(5) |
	⌊		13(2) ⌋	⌊		18(5) ⌋

Principal axes of $\underline{L}$

r.m.s. Amplitude		Direction cosines (x10^3)				
8.1°	887	413	-206	9.3° 198	-939	283
3.3	37	377	925	3.4 543	-136	-829
2.3	460	-828	321	3.2 816	317	482

Principal axes of reduced $\underline{T}$

r.m.s. Amplitude		Direction cosines (x10^3)				
0.20 Å	-738	-661	132	0.20 Å -267	888	-373
0.18	-166	372	914	0.18 -232	316	920
0.18	-656	650	-383	0.16 935	332	122

Displacement of axes from intersecting (Å)

Parallel to $\underline{L}_1$	0.37	0.89
Parallel to $\underline{L}_2$	-0.08	0.68
Parallel to $\underline{L}_3$	0.26	0.09

Effective screw translations (Å)

Parallel to $\underline{L}_1$	0.015	-0.032
Parallel to $\underline{L}_2$	-0.008	0.066
Parallel to $\underline{L}_3$	-0.041	0.023

Fractional coordinates of unique origin (x10^4)

$\underline{x}$	8888	7840
$\underline{y}$	4804	2548
$\underline{z}$	4668	5470

Fractional coordinates of centre of gravity (x10^4)

$\underline{x}$	9889	8332
$\underline{y}$	5606	1038
$\underline{z}$	4304	6163

r.m.s. $\Delta\underline{U}_{11}$	0.0023	0.0036 Å^2

[1]Axes of reference are orthogonal angstrom axes. E.s.d.'s of components of $\underline{L}$ are given in parentheses in units of the last places shown.

also noted in Part 1). Examination of the individual $\Delta \underline{U}_{11}$ shows significant independent motion of the phenyl groups and also of atoms in the five-membered ring. The r.m.s. $\Delta \underline{U}_{11}$ values of 0.0023 and 0.0036 $\overset{\circ}{A}{}^2$ for the analyses of the phenyl groups indicate that these groups do behave as rigid bodies. Both groups show nearly isotropic translational motion and anisotropic librational motion. The principal axes of $\underline{L}$ are oriented as expected: the largest axes, $\underline{L}_1$, correspond to rotations about the B-C bonds, the angles between the $\underline{L}_1$ axes and the bonds being 6.9° (C(3)) and 2.6° (C(9)). The unique origins are in expected locations, for the C(3)-C(8) ring approximately at C(3), and for the C(9)-C(14) ring near C(9).

The appropriate bond distances and angles in the phenyl groups have been corrected for libration (15,16) using shape parameters $\underline{q}^2$ of 0.08 for all atoms. Riding motion corrections based on the $\Delta \underline{U}_{11}$ (26,27) have been applied to the C-F bonds. Both corrected and uncorrected bond lengths and angles appear in Tables 15 and 16.

RESULTS AND DISCUSSION

Figure 4 shows a general view of the molecule and the crystallographic numbering scheme. Figures 5 and 6 show the packing arrangement viewed along $\underline{b}$ and $\underline{c}$ respectively. Intra-annular torsion angles defining the conformation of the boroxazolidine ring are given in Table 17 and some weighted least-squares mean planes in Table 18. Non-bonded intra- and intermolecular distances and details of the hydrogen-bonding
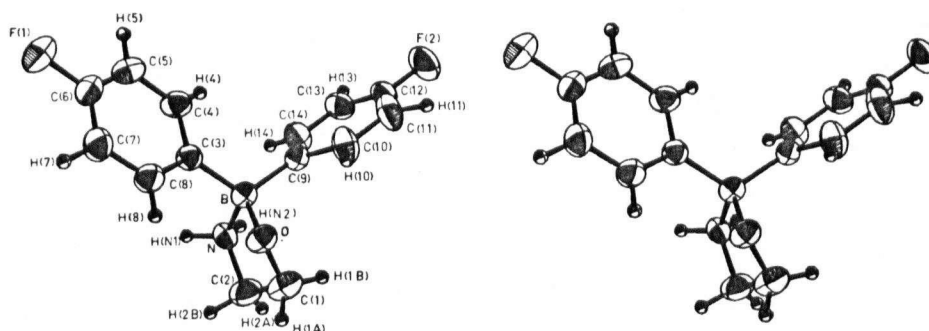
Figure 4

A stereo view of the molecule showing 50%
probability thermal motion ellipsoids for
the non-hydrogen atoms and the
crystallographic numbering of the atoms.

scheme appear in table 19.

The crystal structure consists of discrete molecules of
B,B-bis(p-fluorophenyl)boroxazolidine, each linked to six
others by an extensive and interesting network of hydrogen
bonds. O...H-N (O...N = 2.941(3) Å) and weak F...H-N (F...N =
3.171(4) Å) hydrogen bonds form continuous spirals about
alternate twofold screw axes along c, thereby forming 'nets'
of molecules normal to the a axis. The hydrogen bonding
scheme is completed by a weak F...H-C (F...C = 3.318(5) Å)
interaction which forms spirals about alternate twofold screw
axes along b, linking adjacent 'nets' to form a three-
dimensional network which employs all available acceptors in
the molecule.

Table 15

Bond lengths (Å) with estimated

standard deviations in parentheses

(a) Non-hydrogen atoms

Atoms	uncorr.	corr.	Atoms	uncorr.	corr.
F(1)-C(6)	1.369(4)	1.372	C(3)-C(8)	1.394(5)	1.407
F(2)-C(12)	1.367(4)	1.370	C(4)-C(5)	1.384(5)	1.387
O-C(1)	1.418(4)	---	C(5)-C(6)	1.369(5)	1.381
O-B	1.471(4)	---	C(6)-C(7)	1.365(5)	1.374
N-B	1.652(4)	---	C(7)-C(8)	1.384(5)	1.387
C(3)-B	1.616(4)	1.619	C(9)-C(10)	1.401(4)	1.416
C(9)-B	1.620(5)	1.623	C(9)-C(14)	1.377(5)	1.388
N-C(2)	1.491(4)	---	C(10)-C(11)	1.385(6)	1.390
C(1)-C(2)	1.494(6)	---	C(11)-C(12)	1.366(6)	1.378
C(3)-C(4)	1.391(5)	1.399	C(12)-C(13)	1.362(6)	1.377
			C(13)-C(14)	1.395(5)	1.400

(b) Bonds involving hydrogen atoms

Atoms	distance	Atoms	distance
N-H(N1)	0.88(4)	C(5)-H(5)	0.91(5)
N-H(N2)	0.98(4)	C(7)-H(7)	1.04(5)
C(1)-H(1A)	0.92(5)	C(8)-H(8)	0.92(4)
C(1)-H(1B)	0.98(4)	C(10)-H(10)	0.93(4)
C(2)-H(2A)	0.94(6)	C(11)-H(11)	0.94(6)
C(2)-H(2B)	0.99(4)	C(13)-H(13)	0.93(5)
C(4)-H(4)	0.99(4)	C(14)-H(14)	1.00(4)

Table 16

Bond angles (deg) with estimated

standard deviations in parentheses

(a) Non-hydrogen atoms

Atoms	uncorr.	corr.
C(1)-O-B	108.2(2)	---
C(2)-N-B	105.5(2)	---
O-B-N	99.9(2)	---
O-B-C(3)	110.4(2)	---
O-B-C(9)	112.9(2)	---
N-B-C(3)	110.7(2)	---
N-B-C(9)	107.7(2)	---
C(3)-B-C(9)	114.2(2)	---
O-C(1)-C(2)	106.0(3)	---
N-C(2)-C(1)	105.0(3)	---
B-C(3)-C(4)	123.3(3)	123.1
B-C(3)-C(8)	120.7(3)	120.6
C(4)-C(3)-C(8)	116.0(3)	116.3
C(3)-C(4)-C(5)	122.8(3)	122.6
C(4)-C(5)-C(6)	118.2(3)	118.1
F(1)-C(6)-C(5)	119.3(3)	119.2
F(1)-C(6)-C(7)	118.7(3)	118.5
C(5)-C(6)-C(7)	121.9(3)	122.2
C(6)-C(7)-C(8)	118.7(3)	118.5
C(3)-C(8)-C(7)	122.3(3)	122.2
B-C(9)-C(10)	119.4(3)	119.2
B-C(9)-C(14)	124.5(3)	124.3
C(10)-C(9)-C(14)	116.1(3)	116.5
C(9)-C(10)-C(11)	121.4(3)	121.2
C(10)-C(11)-C(12)	119.5(3)	119.3
F(2)-C(12)-C(11)	120.0(3)	119.7
F(2)-C(12)-C(13)	118.2(3)	118.1
C(11)-C(12)-C(13)	121.8(3)	122.2
C(12)-C(13)-C(14)	117.6(4)	117.4
C(9)-C(14)-C(13)	123.6(3)	123.4

(b) Angles involving hydrogen atoms

Atoms	value	Atoms	value
B-N-H(N1)	113(2)	C(3)-C(4)-H(4)	117(2)
B-N-H(N2)	117(2)	C(5)-C(4)-H(4)	119(2)
C(2)-N-H(N1)	108(2)	C(4)-C(5)-H(5)	123(3)
C(2)-N-H(N2)	112(2)	C(6)-C(5)-H(5)	118(3)
H(N1)-N-H(N2)	101(3)	C(6)-C(7)-H(7)	119(3)
O-C(1)-H(1A)	106(3)	C(8)-C(7)-H(7)	122(3)
O-C(1)-H(1B)	113(2)	C(3)-C(8)-H(8)	120(2)
C(2)-C(1)-H(1A)	108(3)	C(7)-C(8)-H(8)	117(2)
C(2)-C(1)-H(1B)	104(2)	C(9)-C(10)-H(10)	117(3)
H(1A)-C(1)-H(1B)	119(4)	C(11)-C(10)-H(10)	121(3)
N-C(2)-H(2A)	113(3)	C(10)-C(11)-H(11)	125(4)
N-C(2)-H(2B)	102(2)	C(12)-C(11)-H(11)	115(4)
C(1)-C(2)-H(2A)	115(4)	C(12)-C(13)-H(13)	112(3)
C(1)-C(2)-H(2B)	112(3)	C(14)-C(13)-H(13)	131(3)
H(2A)-C(2)-H(2B)	110(4)	C(9)-C(14)-H(14)	123(2)
		C(13)-C(14)-H(14)	113(2)

Table 17

Intra-annular torsion angles (deg)

in the boroxazolidine ring

Bond	observed		calc.
	a	b	
B-O	-22.2(2)	-32.9(3)	-37.7
O-C(1)	39.6(2)	42.1(3)	43.8
C(1)-C(2)	-39.3(2)	-31.2(3)	-33.3
C(2)-N	24.8(2)	10.2(3)	10.0
N-B	-3.1(2)	12.7(3)	17.2

a. B,B-diphenylboroxazolidine, Part 1

b. This work
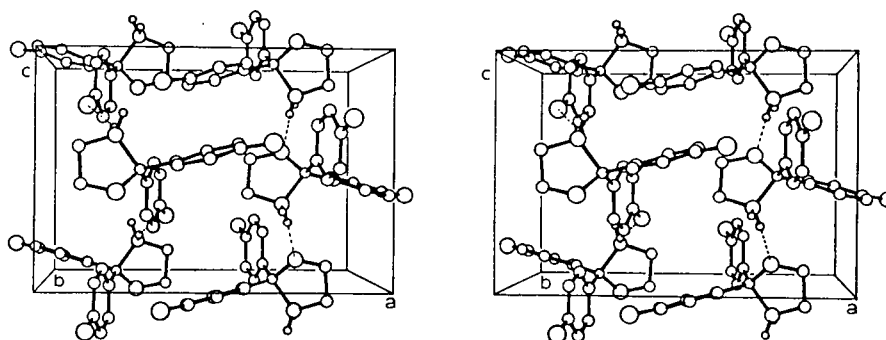
Figure 5

The structure viewed along <u>b</u>, O...H-N and
F...H-N hydrogen bonds are represented by
broken lines.
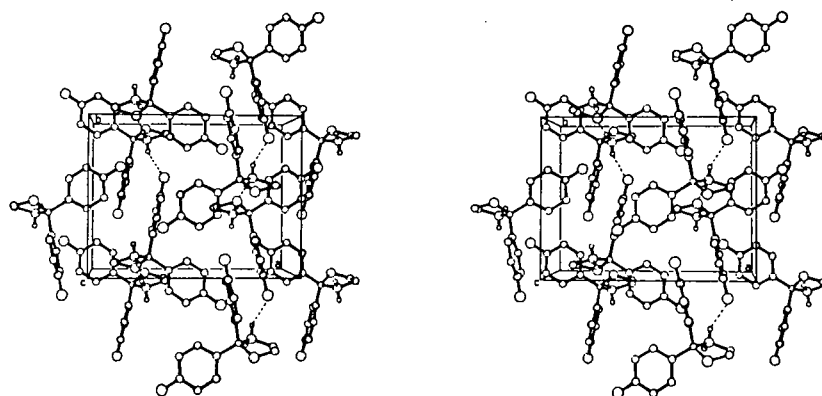
Figure 6

The structure viewed into <u>c</u>, broken lines
represent hydrogen bonds.

The geometrical data for all three hydrogen bonds are quite reasonable, the angles at the hydrogen and at the acceptor atoms are within the expected limits (28). The O...N distance is near the accepted mean while the F...N distance of 3.171 is longer than the mean value of 2.92(11) Å (29) and probably represents a relatively weak interaction. It should be noted, however, that the mean N...F distance is based on only 10 examples, most (if not all) of which occur in inorganic structures in which the interaction is highly ionic in nature. In the present case the N and F atoms carry only small partial charges and evidence indicates that the nitrogen atom in this structure probably carries a net negative charge. These factors are probably responsible for the long N...F distance.

The F...H distances in the F...H-N and F...H-C interactions are 2.35(4) and 2.34(4) Å, both of which are significantly less than the sum of van der Waals radii. The geometry of the F...H-C system is more nearly ideal than that of the F...H-N hydrogen bond and with the F...H distances equal there is little doubt that the F...H-C interaction is a weak hydrogen bond.

Aside from the hydrogen bonds there is only one other intermolecular contact which is significantly less than the sum of van der Waals radii, H(7)...H(13), 2.16(7) Å. All other intermolecular contacts, the shortest of which are listed in Table 19, correspond to normal van der Waals interactions.

The conformation of the five-membered boroxazolidine ring is different from that in 1 as can be seen by comparison of the corresponding dihedral angles in Table 17. The two carbon atoms were on opposite sides of the NBO plane in 1 while in the present structure both C(1) and C(2) lie on the same side of the NBO plane, displaced -0.73 and -0.32 Å from the plane. The observed dihedral angles in the ring are in good agreement with those obtained from energy minimization calculations for ω_1 = 10° (17), also shown in Table 17. The observed magnitudes of the dihedral angles are slightly smaller than the calculated values since the mean valence angle in the ring, 104.9°, is slightly greater than the calculated value of 104.2°, but in good agreement with the mean of 104.8° in 1. The individual values range from 99.7(2) at B to 108.2(2)° at O. There are small but significant differences between the angles at O, N, and C(1) in this structure and in 1 which are a result of conformational and electronic differences. The angular strain inherent in the five-membered ring is, as in 1, partially relieved by a significant shortening of the C(1)-C(2) bond (1.494(6) Å) from the value of 1.537 Å expected for a C($\underline{sp}^3$)-C($\underline{sp}^3$) single bond. The B-N distance of 1.652(4) Å agrees well with chemically similar bonds: 1.653 in 1, 1.647 in triethanolamine borate (20), and 1.638 Å in (Et$_2$NBF$_2$)$_2$ (30).

The two phenyl rings are planar within experimental error (see Table 18). The eight phenyl hydrogen atoms lie in the respective mean planes while the boron and fluorine atoms

Table 18

Weighted least-squares mean planes

(a) Distances (Å) of relevant atoms from the mean planes

Atom	d	d/σ	Atom	d	d/σ
Plane 1: C(3)-C(8)			**Plane 2: C(9)-C(14)**		
C(3)	-0.005	1.6	C(9)	-0.007	2.4
C(4)	0.003	0.8	C(10)	0.010	2.3
C(5)	0.000	0.1	C(11)	0.000	0.0
C(6)	0.000	0.0	C(12)	-0.007	2.1
C(7)	-0.005	1.1	C(13)	0.007	1.6
C(8)	0.008	2.0	C(14)	0.004	1.0
B	-0.031	9.5	B	-0.059	18.4
F(1)	-0.059	24.1	F(2)	-0.008	3.1
H(4)	0.091	2.4	H(10)	-0.004	0.1
H(5)	-0.128	2.5	H(11)	0.123	2.0
H(7)	0.039	0.8	H(13)	-0.003	0.1
H(8)	0.005	0.1	H(14)	0.079	2.0

(b) Equations of planes: $\underline{l}X + \underline{m}Y + \underline{n}Z = \underline{p}$, where $\underline{X}$, $\underline{Y}$, and $\underline{Z}$ are orthogonal angstrom coordinates derived as follows:

$$\begin{bmatrix} \underline{X} \\ \underline{Y} \\ \underline{Z} \end{bmatrix} = \begin{bmatrix} \underline{a} & 0 & 0 \\ 0 & \underline{b} & 0 \\ 0 & 0 & \underline{c} \end{bmatrix} \begin{bmatrix} \underline{X} \\ \underline{Y} \\ \underline{Z} \end{bmatrix}$$

Plane	$\underline{l}$	$\underline{m}$	$\underline{n}$	$\underline{p}$
1	-0.2755	0.1068	-0.9554	-6.8546
2	-0.9743	-0.2217	-0.0395	-11.3654

The dihedral angle between plane normals is 74°

are significantly displaced from the planes, F(1) and B by -0.06 and -0.03 Å from the C(3)-C(8) plane and F(2) and B by -0.01 and -0.06 Å from the C(9)-C(14) plane. This is probably a result of intra- and intermolecular steric forces. The dihedral angle between the plane normals is 74° compared to 100° in 1. The two fluorophenyl groups are not equivalent, the rings being unequally rotated about the B-C bonds. The dihedral angles C(8)[C(3)-B]O and C(10)[C(9)-B]O are 21.7(3) and 30.2(3)° compared to values of 78.0(2) and 7.0(2)° in 1. The difference in the orientation of the phenyl groups in the two structures is a result of packing considerations, among which the C(14)-H(14)...F(1) hydrogen bond may be an important factor.

The corrected C-C bond lengths in the phenyl groups range from 1.374 to 1.416 Å with a mean value of 1.390 Å. There is a significant variation in the individual bond distances, the bond lengths decreasing as they are removed from the boron substituent. The mean values for the three groups are 1.403, 1.391, and 1.378 Å, similar to the corresponding values for 1 (corrected for libration) of 1.403, 1.394, and 1.380 Å. The B-C distances, mean 1.621, are slightly longer than the value of 1.616 Å in 1 and shorter than in the tetraphenyl borate anion (1.631-1.648 (8) Å) (19).

The angles in the phenyl rings have a mean value of 120° but the individual values, ranging from 116.3 to 123.4°, show significant deviations from 120°. The mean angle at the carbon atom carrying the boron substituent is 116.4° and the

other mean values are 122.4, 118.3, and 122.2° for atoms _ortho_ , _meta_ , and _para_ to the boron group respectively. These variations have been explained in terms of the electronegativities of the substituent groups (31). The angles at C(6) and C(12) carrying the fluorine atoms, mean 122.2°, are as expected for an electron withdrawing group. The angles at C(3) and C(9), mean 116.4°, carrying the boron substituent are indicative that this group is releasing electron density into the aromatic system. The distribution of bond lengths is in agreement with this observation, indicating small residual positive charge at atoms _ortho_ to F and negative charge _ortho_ to B, the overall donating and withdrawing effects of the _para_ substituents cancelling each other to result in electronic neutrality of the aromatic π systems. There is both theoretical and physical evidence which indicates that in spite of the N$\rightarrow$B dative bond, the boron atom remains more positively charged than the nitrogen atom as a result of charge redistributions occurring in the remainder of the molecule (30,32). This offers an explanation for the small differences between the B-C, B-O, C-N, C-O, and C(1)-C(2) bond lengths in this structure and those in 1, where the negative charges which occur at the fluorine atoms in this structure result in delocalization effects in the molecule. The mean C-F distance of 1.371 Å is close to that of 1.368 Å in _o_-fluorobenzoic acid (33) but significantly longer than the mean C(ar)-F distance of 1.328 Å in ref. 18.

The mean bond angles at tetrahedrally and trigonally coordinated atoms are 109.4 and 119.9°. There are a number of

Table 19

(a) Selected intra- and intermolecular contacts

Intramolecular		Intermolecular*	
Atoms	distance	Atoms	distance
O...C(8)	2.888(4)	F(1)...F(2)[1]	3.229(4)
O...C(10)	2.961(4)	F(1)...C(11)[2]	3.484(5)
N...C(14)	3.084(4)	F(1)...C(12)[1]	3.400(4)
N...C(8)	3.489(4)	F(1)...N[3]	3.446(4)
		F(2)...C(7)[4]	3.451(5)
		C(6)...C(11)[2]	3.477(5)
		C(1)...H(N2)[5]	2.96(4)
		C(5)...H(11)[2]	2.98(7)
		C(6)...H(11)[2]	2.79(7)
		C(6)...H(14)[3]	2.88(4)
		C(7)...H(13)[6]	2.99(5)
		C(13)...H(11)[7]	2.92(6)
		C(13)...H(7)[4]	2.94(5)
		H(7)...H(13)[6]	2.16(7)

(b) Hydrogen-bond data (distances in Å and angles in deg)

D-H...A	H...A	D...A	∠DHA	∠XAH
N-H(N2)...O[8]	1.96(5)	2.941(3)	176(4)	122(1),129(1)
N-H(N1)...F(2)[7]	2.35(4)	3.171(4)	155(3)	140(1)
C(14)-H(14)...F(1)[9]	2.34(4)	3.318(5)	165(3)	99(1)

*Superscripts refer to atoms at positions:

[1]	1/2-x	1/2-y	1-z	[6]	x	1+y	z
[2]	2-x	1/2+y	3/2-z	[7]	3/2-x	-y	z-1/2
[3]	2-x	1/2+y	1/2-z	[8]	3/2-x	1-y	z-1/2
[4]	x	y-1	z	[9]	2-z	y-1/2	1/2-z
[5]	3/2-x	1-y	1/2+z				

significant deviations from the mean values resulting from steric and electronic effects. Interior angles in the rings have already been discussed. Asymmetry of the packing appears to be responsible for significant differences between corresponding angle pairs O-B-C, N-B-C, and C-C-F. The C(3)-B-C(9) angle is equal to that in 1 to within experimental error.

The mean C($\underline{sp}^3$)-H, C(ar)-H, and N-H distances of 0.95, 0.96, and 0.93 Å are as expected for X-ray data. The bond angles involving the hydrogen atoms are generally as expected. There are significant differences between the C-C-H angles at C(13) and C(14) which are probably a result of van der Waals contacts F(1)...H(14) and H(7)...H(13) (see Table 19).

PART 3

CRYSTAL AND MOLECULAR STRUCTURE OF
4,4-DIMETHYL-2,2-DIPHENYL-1,3-DIOXA-
4-AZONIA-2-BORANATACYCLOPENTANE

INTRODUCTION

From the reaction of N-hydroxydialkylamine (1) and formaldehyde an addition can be expected either at the nitrogen or at the oxygen atom to give 2 or 4. The addition products, originally regarded as N-hydroxymethyl-oxydialkylamines (4) by Zinner and Ritter (34,35), react with diphenylboron-supplying reagents (Ph$_2$B-X) to yield crystalline compounds which were initially assigned the structure 5 containing intramolecular N→B coordination. This assignment was based on the earlier studies of the 'boroxazolidines' by Weidmann and Zimmerman (36-38) and was subsequently employed for compounds of this type (39-43).

R = CH$_3$
Ph = C$_6$H$_5$
X = a) O-BPh$_2$
   b) Ph
   c) O-CH$_2$-CH$_2$-NH$_2$
   d) O-CH$_2$-CH$_2$-N(CH$_3$)$_2$

There is, however, some evidence which indicates that the alternate structures 2 and 3 are probably favored over

the originally proposed structures 4 and 5:

1. The alkylation of N-hydroxydialkylamines normally leads to tertiary amine oxides.

2. N-Oxides show stronger basicity and possess better nucleophilic or donor qualities than the isomeric N-alkyloxyamines (44,45). A hydrogen bridge chelate of the type 2 should therefore be more stable than 4.

3. If both forms 2 and 4 existed, possibly in a state of equilibrium, the reaction with an electrophilic reagent such as Ph_2B-X should shift the (hypothetical) equilibrium to the side of the better donor molecule, i.e. the N-oxide (2).

4. The N-oxide form not only facilitates the approach of the Lewis acid Ph_2B-X to the donor (oxygen) atom but also results in a sterically favored chelate structure (3).

5. Ethanolamine esters of diphenylborinic acid are intramolecular N→B coordinated cyclic complexes (6), as recently proved conclusively for $Ph_2B-O-CH_2CH_2NH_2$ (Part 1) and $(p-FC_6H_4)_2B-O-CH_2CH_2NH_2$ (Part 2). Despite the stability of these 'boroxazolidines' (9,36-38) the rechelation of the applied examples (6, R = H, CH_3) was possible with the formaldehyde adduct. This also

supports structures 2 and 3 since it is not very plausible that a weakly basic N-hydroxymethyl-oxydialkylamine $HO-CH_2ONR_2$ (4) in an equimolar quantity can displace the isosteric but more basic aminoalcohol $HO-CH_2CH_2NR_2$.

6. Finally there exists an analogy between 3 and the diphenyl boron chelates (7) of N-(2-hydroxyalkyl)-dialkylamine-N-oxides and other similar cyclic boron-nitrogen-betaines (46-50) which are closely related to 3 both in means of preparation and in their chemical and physical behavior.

These considerations and also the chemical and physical data obtained to date are consistent with the betaine-type chelate 3, but do not provide unambiguous proof. To this end the full X-ray crystallographic study of the homologue with R = CH_3 has been carried out.

EXPERIMENTAL

4,4- Dimethyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-boranatacyclopentane (3)

A solution of N-hydroxydimethylamine (5 mmole) in 5 ml of ethanol was mixed with an aqueous solution of formaldehyde (40%, 5 mmole). After addition of:

a) 2.5 mmole oxybisdiphenylborane or

b) 5.0 mmole triphenylborane or

c) 5.0 mmole $\underline{B}$-(2-aminoethyloxy)diphenylborane or

d) 5.0 mmole $\underline{B}$-(2-dimethylaminoethyloxy)diphenylborane

the mixture was heated until initial boiling and then allowed to cool. During the cooling or after the dissolution of the boron component the precipitation began.

Yields: a) 99%, b) 90%, c) 98%, d) 85%

m.p. 191-192° C   (acetonitrile);   Lit.   (6):   m.p.   191-192° (ethanol)

$C_{15}H_{18}BNO_2$ (255.1) Calc. C 70.62 H 7.11 B 4.24 N 5.49

Found   70.96   7.21   4.18 , 5.45

^{1}H-NMR (100 MHz, d_6-DMSO/TMS) τ (ppm):   6.84 s   (6, CH_3), 5.25 s (2, CH_2), 2.6-3.1 m (10, Ph)

^{11}B-NMR (32.1 MHz, DMSO): δ(BF_3OEt_2) = -11.1 ppm

Crystals suitable for X-ray analysis were obtained by recrystallization from 3:1 acetone-carbon tetrachloride. The crystal used for data collection was bounded by the (001), (010), and (100) planes at distances of 0.14, 0.35, and 0.14 mm from an internal origin and was mounted with $\underline{b}$ parallel to the goniostat axis. Unit-cell and space group data were obtained from film and diffractometer measurements. The unit-cell parameters were refined by a least-squares treatment of $\sin^2\theta$ values for 27 reflexions measured on a diffractometer with Cu K_α radiation. Crystal data are:
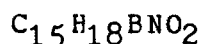
$C_{15}H_{18}BNO_2$ f.w. = 255.1

Orthorhombic, $\underline{a}$ = 17.043(3), $\underline{b}$ = 6.289(1), $\underline{c}$ = 13.024(2) Å, $\underline{V}$ = 1395.9(5) Å^3, $\underline{Dm}$ = 1.225(flotation in aqueous KI), $\underline{Z}$ = 4, $\underline{Dx}$ = 1.214(1) g cm^{-3}, $\underline{F}$(000) = 544 (20° C, Cu K$_\alpha$, λ = 1.5418 Å, μ = 6.4 cm^{-1}). Absent reflexions: $0\underline{k}\underline{\ell}$, $\underline{k}$ + $\underline{\ell}$ $\neq$ $2\underline{n}$ and $\underline{h}0\underline{\ell}$, $\underline{h}$ $\neq$ $2\underline{n}$, space group $\underline{Pna}2_1$ ($\underline{C}_{2\underline{v}}^9$, No. 33).

Intensities were measured on a Datex-automated General Electric XRD 6 diffractometer, with a scintillation counter, Cu K$_\alpha$ radiation (nickel filter and pulse height analyser), and a θ-2θ scan at 2° min^{-1} over a range of (1.80 + 0.86 tan θ) degrees in 2θ, with 20 s background counts being measured at each end of the scan. Data were measured to 2θ = 145° (minimum interplanar spacing 0.81 Å). The r.m.s. deviation of the intensity of the check reflexion, measured every 40 reflexions throughout the data collection, from its initial value was 2.4%. The final intensity was 1.045 times the initial value. Lorentz, polarization, and absorption corrections were applied, and structure amplitudes were derived. Of 1450 independent reflexions measured, 324 had intensities less than $3\sigma(\underline{I})$ above background where $\sigma^2(\underline{I})$ = $\underline{S}$ + $\underline{B}$ + $(0.06\underline{S})^2$ with $\underline{S}$ = scan count and $\underline{B}$ = background count, corrected to time of scan. These reflexions were not included in the refinement.

Structure Analysis

The space group was assumed to be $\underline{Pna}2_1$ from systematic absences and the number of molecules in the unit-cell ($\underline{Z}$ =

4). The structure was solved by direct methods, 158 reflexions with normalized structure factor $|E| \geq 1.55$ being used in the symbolic addition procedure for non-centrosymmetric crystals (21). The phases of the 5 5 0, 8 3 0, and 14 2 1 reflexions were fixed to define the origin and the enantiomorph was fixed by allowing one of the symbol phases to take only values between 0 and 500 mc. During a manual expansion, carried out among the 75 reflexions with largest $|E|$ values, it became apparent that there were eight reflexions from which the three symbol phases could be chosen. After several unsuccessful runs, a combination of symbol phases which gave a promising set of trial phases was found. The three symbol phases; 1 1 11, 3 1 13, and 1 4 8; along with the origin determining phases comprise the basic starting group given in Table 20.

Eight starting sets were generated by allowing symbols $\underline{a}$ and $\underline{b}$ to have initial values of ±250 mc and $\underline{c}$ to have initial values of 125 and 375 mc (thereby fixing the enantiomorph). These sets were used as input to a computer program which determines phases using the tangent formula (22,23). The values of overall $\underline{t}$, overall $\propto$, Q, and $\underline{Rk}$ on the final cycle for each of the sets are given in Table 21. Set 4, which had the lowest value of $\underline{Rk}$, was expanded to 185 reflexions with $|E| \geq 1.50$ by starting with the same symbol values as in set 4. The final value of $\underline{Rk}$ was 0.23 with 180 phases assigned. An $\underline{E}$-map based on these 180 phases gave positions for the 19 non-hydrogen atoms among the 40 highest peaks.

Table 20

Basic starting set of reflexions for $C_{15}H_{18}BNO_2$

$\underline{h}$	$\underline{k}$	$\underline{\ell}$	$|\underline{E}|$	phase (mc)
5	5	0	3.28	0 ⌐
8	3	0	2.07	0 ⊢ origin determining
14	2	1	1.99	0 ⌙
1	1	11	2.66	$\underline{a}$
3	1	13	2.62	$\underline{b}$
1	4	8	2.44	$\underline{c}$

Table 21

Results for the eight starting sets

in the phase determination procedure

Set	$\underline{a}$(mc)	$\underline{b}$(mc)	$\underline{c}$(mc)	$\underline{t}$	α	$\underline{Q}$	$\underline{Rk}$	$\underline{N}$
1	250	250	125	0.69	158	0.30	0.30	146
2	250	250	375	0.72	158	0.27	0.31	144
3	250	-250	125	0.69	165	0.30	0.35	141
4	250	-250	375	0.68	160	0.31	0.24	154
5	-250	250	125	0.69	160	0.30	0.30	145
6	-250	250	375	0.71	163	0.28	0.34	143
7	-250	-250	125	0.71	163	0.28	0.28	149
8	-250	-250	375	0.58	135	0.41	0.36	141

Two cycles of full-matrix least-squares refinement of the positional and isotropic thermal parameters of the non-hydrogen atoms gave R 0.156. This was followed by two cycles of anisotropic refinement which reduced $\underline{R}$ to 0.103. A difference map at this point revealed the positions of seven of the ten phenyl hydrogen atoms. The remaining hydrogen atom positions were calculated and all 18 hydrogen atoms were included in subsequent cycles of refinement with isotropic thermal parameters. The refinement was concluded at $\underline{R}$ 0.071 for 1100 reflexions with $\underline{I} > 3\sigma(\underline{I})$ (26 reflexions were given zero weight in the final stages of refinement due to suspected extinction or counter errors).

The scattering factors for the non-hydrogen atoms were taken from ref. 12 and those for the hydrogen atoms from ref. 13. The weighting scheme: $\underline{w} = 1/\sigma^2(\underline{F})$ where $\sigma^2(\underline{F})$ is derived from the previously defined $\sigma^2(\underline{I})$, gave constant average values of $\underline{w}(\underline{F}o-\underline{F}c)^2$ over ranges of $|\underline{F}o|$ and was employed in the final stages of refinement. On the final cycle of refinement no parameter shift was greater than 0.33σ for non-hydrogen atoms except for the $\underline{y}$ coordinates of methyl carbon atoms C(2) and C(3) which shifted by 0.80σ. The shifts were less than 1.5σ for the methyl hydrogens and less than 1.0σ for the remaining hydrogen atoms. The final positional and thermal parameters appear in Tables 22 and 23 respectively. Observed and calculated structure amplitudes are available on request.

THERMAL MOTION AND CORRECTION OF MOLECULAR GEOMETRY

Table 22

Final positional parameters (fractional x 10^4, x 10^3 for H atoms)

with estimated standard deviations in parentheses

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$
O(1)	3418(2)	4469(6)	1466(4)
O(2)	3126(2)	962(6)	915
N	3315(2)	977(7)	1968(4)
C(1)	3207(4)	3249(14)	2300(6)
C(2)	4138(4)	108(17)	2051(7)
C(3)	2771(5)	-431(22)	2513(6)
C(4)	2139(3)	3904(9)	385(4)
C(5)	1578(4)	2389(11)	255(7)
C(6)	801(3)	2872(13)	39(7)
C(7)	571(3)	4941(11)	-20(5)
C(8)	1100(3)	6539(13)	91(6)
C(9)	1907(3)	6006(10)	308(5)
C(10)	3584(3)	3654(9)	-463(5)
C(11)	3659(3)	1995(10)	-1166(5)
C(12)	4062(4)	2244(13)	-2085(6)
C(13)	4409(4)	4265(14)	-2305(6)
C(14)	4327(4)	5879(14)	-1610(7)
C(15)	3922(3)	5542(12)	-688(6)
B	3054(3)	3323(11)	570(5)
H(1A)	354(4)	364(11)	307(6)
H(1B)	255(4)	340(12)	255(5)
H(2A)	434(5)	129(11)	159(8)
H(2B)	422(9)	2(21)	298(14)
H(2C)	425(5)	-177(14)	170(7)
H(3A)	242(11)	-13(29)	228(16)
H(3B)	311(4)	-248(10)	226(5)
H(3C)	285(7)	-43(16)	336(10)
H(5)	170(3)	99(9)	23(4)
H(6)	47(3)	149(7)	-25(4)
H(7)	5(4)	525(11)	-25(5)
H(8)	91(3)	796(9)	12(4)
H(9)	220(6)	706(17)	53(8)
H(11)	342(5)	50(12)	-116(7)
H(12)	404(3)	129(9)	-259(5)
H(13)	479(5)	459(11)	-292(7)
H(14)	443(6)	776(13)	-186(7)
H(15)	384(4)	685(10)	-33(5)

Table 23

Final thermal parameters and

their estimated standard deviations

(a) Anisotropic thermal parameters ($\underline{U}_{11}$ x 100 $\mathring{A}^2$)

Atom	$\underline{U}_{11}$	$\underline{U}_{22}$	$\underline{U}_{33}$	$\underline{U}_{12}$	$\underline{U}_{13}$	$\underline{U}_{23}$
O(1)	4.7(2)	7.5(3)	4.6(2)	-1.2(2)	-1.3(2)	0.3(2)
O(2)	4.6(2)	6.8(3)	3.8(2)	-0.4(2)	-1.0(2)	0.3(2)
N	3.5(2)	6.0(3)	3.4(2)	0.2(2)	-0.5(2)	0.5(2)
C(1)	6.7(4)	10.1(6)	5.7(4)	-0.1(4)	-0.9(3)	0.3(4)
C(2)	4.8(3)	14.2(7)	6.0(4)	3.9(4)	-1.8(3)	-0.4(5)
C(3)	6.5(4)	18.7(11)	4.6(4)	-3.3(6)	1.4(3)	2.6(5)
C(4)	3.7(2)	5.9(3)	3.3(2)	-1.1(2)	0.1(2)	-0.1(2)
C(5)	5.1(3)	4.4(4)	10.4(5)	0.3(2)	-1.9(3)	1.4(4)
C(6)	3.8(3)	8.7(5)	10.1(5)	-1.1(3)	-1.8(3)	1.1(4)
C(7)	3.4(2)	8.0(4)	4.7(3)	0.2(3)	-0.6(2)	0.0(3)
C(8)	4.5(3)	8.4(5)	6.6(4)	2.3(3)	-0.5(3)	-1.3(3)
C(9)	3.9(3)	5.7(4)	5.8(3)	0.4(2)	-0.4(2)	-0.5(3)
C(10)	2.9(2)	6.7(3)	4.2(3)	0.3(2)	-1.1(2)	1.1(3)
C(11)	4.1(3)	5.6(4)	4.9(3)	0.9(2)	-0.3(2)	0.5(3)
C(12)	5.3(3)	8.5(5)	5.8(4)	2.9(3)	0.2(3)	0.6(4)
C(13)	3.9(3)	12.3(6)	6.0(4)	1.2(4)	1.3(3)	1.4(4)
C(14)	4.5(3)	9.1(5)	8.6(5)	0.0(3)	1.7(3)	2.9(4)
C(15)	4.1(3)	7.5(4)	5.6(3)	-1.0(3)	-0.8(2)	1.1(3)
B	3.7(3)	5.2(3)	4.2(3)	-0.7(2)	-0.5(2)	0.3(3)

(b) Isotropic thermal parameters

Atom	$\underline{B}(\mathring{A}^2)$	Atom	$\underline{B}(\mathring{A}^2)$
H(1A)	3.8(16)	H(6)	2.0(9)
H(1B)	5.3(15)	H(7)	5.1(13)
H(2A)	6.0(18)	H(8)	3.1(11)
H(2B)	15.0(44)	H(9)	11.9(27)
H(2C)	8.8(21)	H(11)	5.6(16)
H(3A)	22.2(67)	H(12)	3.0(12)
H(3B)	4.3(14)	H(13)	7.1(17)
H(3C)	11.2(30)	H(14)	9.2(25)
H(5)	2.5(9)	H(15)	4.4(13)
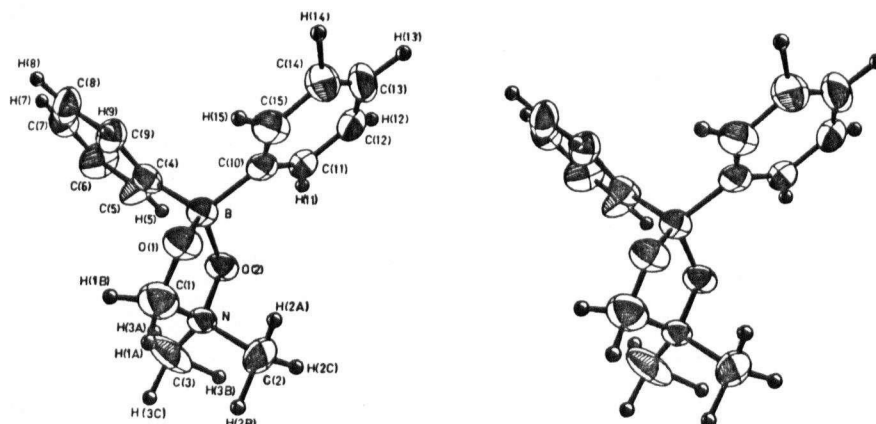
Figure 7

A stereoscopic view of the molecule showing crystallographic numbering scheme. 50% probability ellipsoids are shown for the non-hydrogen atoms.

The ellipsoids of thermal motion for the non-hydrogen atoms are shown in Figure 7. The thermal motion has been analysed in terms of the rigid-body modes of translation ($\underline{T}$), libration ($\underline{L}$), and screw ($\underline{S}$) motion using the computer program $\underline{MGTLS}$ (14). Four analyses were carried out: the 19 non-hydrogen atoms were considered first; then each of the phenyl groups along with the boron atom; and finally the five-membered ring and attached carbon atoms which failed to give a positive-definite $\underline{L}$ tensor. The results of the analyses of the two phenyl groups appear in Table 24.

The r.m.s. standard deviation in the temperature factors $\underline{U}_{11}$ is 0.0035 Å² which indicates that the molecule as a whole (r.m.s. $\Delta\underline{U}_{11}$ = 0.0124 Å²) is not a good rigid-body whereas the thermal motion of the phenyl groups is adequatly

Table 24

Rigid-body thermal parameters[1]

	C(4)-C(9), B			C(10)-C(15), B		
$\underline{L}$ (deg²)	⌈104(17)	-18(7)	26(10)⌉	⌈ 23(9)	-2(5)	-12(9) ⌉
	ǀ	9(7)	-5(5) ǀ	ǀ	13(6)	0(6) ǀ
	⌊		17(5) ⌋	⌊		33(14)⌋

Principal axes of $\underline{L}$

r.m.s.	Amplitude	Direction cosines (x10³)					
10.7°	949	-171	264	6.4°	-562	26	827
3.0	268	2	-963	4.0	-702	512	-495
2.5	165	985	48	3.5	-436	-859	-269

Principal axes of reduced $\underline{T}$

r.m.s.	Amplitude	Direction cosines (x10³)					
0.22 Å	45	-998	36	0.22 Å	152	-857	-492
0.19	998	46	32	0.20	407	508	-759
0.17	-33	35	999	0.14	901	-84	426

Displacement of axes from intersecting (Å)

Parallel to $\underline{L}_1$	0.74	1.60
Parallel to $\underline{L}_2$	0.13	0.55
Parallel to $\underline{L}_3$	0.40	-0.03

Effective screw translations (Å)

Parallel to $\underline{L}_1$	0.014	0.002
Parallel to $\underline{L}_2$	-0.005	0.000
Parallel to $\underline{L}_3$	-0.053	-0.004

Fractional coordinates of unique origin (x10⁴)

$\underline{x}$	2412	3051
$\underline{y}$	4353	3786
$\underline{z}$	329	-388

Fractional coordinates of centre of gravity (x10⁴)

$\underline{x}$	1572	3871
$\underline{y}$	4296	3851
$\underline{z}$	227	-1132

r.m.s. $\Delta \underline{U}_{11}$	0.0052	0.0046 Å²

[1]Axes of reference are orthogonal angstrom axes. E.s.d.'s of components of $\underline{L}$ are given in parentheses in units of the last places shown.

described by the rigid-body parameters (r.m.s. $\Delta \underline{U}_{ij}$ = 0.0052 and 0.0046 Å^2). Both groups show somewhat anisotropic translational motion and anisotropic librational motion, particularly the C(4)-C(9), B group (see Table 24). The principal axes of $\underline{L}$ are oriented as expected: the largest oscillations, $\underline{L}_1$, correspond to rotations about the B-C bonds, the angles between the $\underline{L}_1$ axes and the B-C bonds being 7.3 (C(4)) and 8.9° (C(10)). The unique origins (14) are in the expected locations for both groups, lying between the B and attached phenyl C atoms.

The appropriate bond distances and angles in the phenyl groups have been corrected for libration (15,16) using shape parameters $\underline{q}^2$ of 0.08 for all atoms. Both corrected and uncorrected bond lengths and angles appear in Tables 25 and 26 respectively.

RESULTS AND DISCUSSION

The X-ray analysis has shown that the betaine-type structure (3) is correct. Figure 7 shows a general view of the molecule and the crystallographic numbering scheme. Figure 8 shows the packing arrangement viewed along $\underline{b}$. Intra-annular torsion angles defining the conformation of the five-membered ring are given in Table 27 and some weighted least-squares mean planes through the molecule in Table 28. Non-bonded intra- and intermolecular contacts are listed in Table 29. Henceforth, the molecules $(C_6H_5)_2BOCH_2CH_2NH_2$ and $(\underline{p}-FC_6H_4)_2BOCH_2CH_2NH_2$ (Parts 1 and 2) will be referred to as $\underline{6a}$

Table 25

Bond lengths (Å) with estimated

standard deviations in parentheses

(a) Non-hydrogen atoms

Atoms	uncorr.	corr.	Atoms	uncorr.	corr.
O(1)-C(1)	1.378(9)	---	C(5)-C(6)	1.388(9)	1.391
O(2)-N	1.409(5)	---	C(6)-C(7)	1.361(10)	1.377
O(1)-B	1.506(7)	---	C(7)-C(8)	1.359(10)	1.372
O(2)-B	1.556(8)	---	C(8)-C(9)	1.443(8)	1.446
C(4)-B	1.620(7)	1.624	C(10)-C(11)	1.394(8)	1.402
C(10)-B	1.634(8)	1.639	C(10)-C(15)	1.353(9)	1.363
C(1)-N	1.505(10)	---	C(11)-C(12)	1.390(9)	1.396
C(2)-N	1.509(7)	1.551*	C(12)-C(13)	1.431(10)	1.441
C(3)-N	1.467(9)	1.520*	C(13)-C(14)	1.367(11)	1.374
C(4)-C(5)	1.360(8)	1.373	C(14)-C(15)	1.401(10)	1.406
C(4)-C(9)	1.383(8)	1.399			

(b) Bonds involving hydrogen atoms

Atoms	distance	Atoms	distance
C(1)-H(1A)	1.18(7)	C(6)-H(6)	1.10(5)
C(1)-H(1B)	1.17(7)	C(7)-H(7)	0.95(7)
C(2)-H(2A)	1.02(9)	C(8)-H(8)	0.95(6)
C(2)-H(2B)	1.22(18)	C(9)-H(9)	0.88(11)
C(2)-H(2C)	1.28(9)	C(11)-H(11)	1.02(8)
C(3)-H(3A)	0.70(20)	C(12)-H(12)	0.89(6)
C(3)-H(3B)	1.45(6)	C(13)-H(13)	1.05(9)
C(3)-H(3C)	1.11(13)	C(14)-H(14)	1.24(8)
C(5)-H(5)	0.90(5)	C(15)-H(15)	0.96(6)

*riding motion correction only.

Table 26

Bond angles (deg) with estimated standard deviations in parentheses

(a) Non-hydrogen atoms

Atoms	uncorr.	Atoms	uncorr.	corr.
C(1)-O(1)-B	103.8(4)	B-C(4)-C(5)	122.5(5)	122.1
N-O(2)-B	107.1(4)	B-C(4)-C(9)	120.1(4)	119.9
O(2)-N-C(1)	105.0(4)	C(9)-C(4)-C(5)	117.4(5)	118.0
O(2)-N-C(2)	106.4(4)	C(4)-C(5)-C(6)	122.8(6)	122.5
O(2)-N-C(3)	108.8(5)	C(5)-C(6)-C(7)	119.7(6)	119.5
C(1)-N-C(2)	115.9(6)	C(6)-C(7)-C(8)	120.7(5)	121.2
C(1)-N-C(3)	110.9(7)	C(7)-C(8)-C(9)	118.8(6)	118.5
C(2)-N-C(3)	109.6(7)	C(8)-C(9)-C(4)	120.5(6)	120.3
O(1)-B-O(2)	101.5(4)	B-C(10)-C(11)	119.7(5)	119.6
O(1)-B-C(4)	113.8(5)	B-C(10)-C(15)	121.8(5)	121.7
O(1)-B-C(10)	110.5(4)	C(15)-C(10)-C(11)	118.4(6)	118.5
O(2)-B-C(4)	109.5(4)	C(10)-C(11)-C(12)	121.8(6)	121.7
O(2)-B-C(10)	108.4(4)	C(11)-C(12)-C(13)	118.5(7)	118.5
C(4)-B-C(10)	112.4(4)	C(12)-C(13)-C(14)	119.0(6)	119.1
O(1)-C(1)-N	105.7(6)	C(13)-C(14)-C(15)	120.4(7)	120.3
		C(14)-C(15)-C(10)	121.9(7)	121.9

(b) Angles involving hydrogen atoms

Atoms	value	Atoms	value
O(1)-C(1)-H(1A)	116(4)	C(5)-C(6)-H(6)	113(2)
O(1)-C(1)-H(1B)	115(3)	C(7)-C(6)-H(6)	126(2)
N-C(1)-H(1A)	112(4)	C(6)-C(7)-H(7)	118(4)
N-C(1)-H(1B)	106(4)	C(8)-C(7)-H(7)	120(4)
H(1A)-C(1)-H(1B)	102(5)	C(7)-C(8)-H(8)	118(3)
N-C(2)-H(2A)	90(4)	C(9)-C(8)-H(8)	123(3)
N-C(2)-H(2B)	101(7)	C(8)-C(9)-H(9)	122(7)
N-C(2)-H(2C)	116(4)	C(4)-C(9)-H(9)	116(7)
H(2A)-C(2)-H(2B)	126(9)	C(10)-C(11)-H(11)	130(5)
H(2A)-C(2)-H(2C)	115(6)	C(12)-C(11)-H(11)	108(5)
H(2B)-C(2)-H(2C)	107(8)	C(11)-C(12)-H(12)	123(4)
N-C(3)-H(3A)	100(16)	C(13)-C(12)-H(12)	118(4)
N-C(3)-H(3B)	100(2)	C(12)-C(13)-H(13)	126(4)
N-C(3)-H(3C)	114(6)	C(14)-C(13)-H(13)	115(4)
H(3A)-C(3)-H(3B)	119(17)	C(13)-C(14)-H(14)	121(4)
H(3A)-C(3)-H(3C)	122(17)	C(15)-C(14)-H(14)	116(4)
H(3B)-C(3)-H(3C)	100(6)	C(14)-C(15)-H(15)	126(4)
C(4)-C(5)-H(5)	121(3)	C(10)-C(15)-H(15)	111(4)
C(6)-C(5)-H(5)	115(3)		

Table 27

Intra-annular torsion angles (deg)

Five-membered ring

Bond	obs.	calc.
B-O(1)	34.3(5)	36.4
O(1)-C(1)	-42.3(5)	-43.9
C(1)-N	33.7(5)	34.8
N-O(2)	-10.5(5)	-12.3
O(2)-B	-13.4(4)	-15.0

and 6b respectively.

The conformation of the five-membered ring is nearly the same as that of the isosteric 'boroxazolidine' ring in 6b, four of the five torsion angles being equal within experimental error while the last differs by 2.5° (4 standard deviations). Atoms C(1) and N both lie on the same side of the OBO plane, displaced -0.75 and -0.31 Å from the plane. The observed torsion angles in the ring are in good agreement with those obtained from energy minimization calculations for ω_1 = 10° (17), also given in Table 27. The observed magnitudes of the torsion angles are slightly smaller than the calculated values since the mean angle in the ring, 104.6°, is slightly greater than the calculated value of 104.2° but in good agreement with the values of 104.8 and 104.9° in the structures 6a and 6b. The individual values range from 101.5(4) at B to 107.1(4)° at O(2). The angle at B is slightly, but significantly, greater than the mean value of 99.8(1)° in the boroxazolidines.

The bond distances in the five-membered ring differ from their expected values as a result of steric strain and electron distribution in the molecule, analogous to that occurring in systems with N→B interactions (see eg. 12 and 32). The O(1)-C(1) bond, 1.378(9) Å, is significantly shorter than the usual value of 1.426 Å as well as the values of 1.413 in 6a and 1.418 Å in 6b. The C(1)-N bond, 1.505(10) Å, is somewhat longer than those in 6a and 6b (1.485 and 1.491 Å) but is not significantly longer than a normal C(sp^3)-

N($\underline{sp}^3$) bond. The N-O(2) distance of 1.409(5) Å is significantly longer than the sum of covalent radii (1.36 Å) but lies in the range of 1.34-1.44 Å usually observed for N-O single bonds (18,51). The two B-O distances, 1.506(7) and 1.556(8) Å, are significantly different. The pattern of one bond close to the normal value and one on the order of 0.1 Å longer than normal also occurs in the boroxazolidines $\underline{6a}$ and $\underline{6b}$ where B-O distances are 1.484 and 1.471 Å and the B-N bonds are 1.653 and 1.652 Å, each about 0.1 Å longer than normal. The exocyclic C-N distances have been corrected for riding motion and are equal within experimental error. Bearing in mind that the riding model approach usually overcorrects, it still appears that these bonds are somewhat longer than normal (see Table 25).

The two phenyl rings are planar within experimental error (see Table 28). Two hydrogen atoms, H(6) and H(14), are significantly displaced from their respective mean planes, probably as a result of inaccuracy in the hydrogen atom positions due to thermal effects. The boron atom is significantly displaced from both phenyl mean planes, by 0.07 from the C(4)-C(9) plane and by 0.11 Å from the C(10)-C(15) plane, representing a slight folding of the phenyl groups away from each other. The dihedral angle between the mean planes is 74°. The two phenyl groups are not equivalent, the rings being rotated unequally about the B-C bonds. The dihedral angles C(9)[C(4)-B]O(1), C(15)[C(10)-B]O(1), C(5)[C(4)-B]O(2), and C(11)[C(10)-B]O(2) are -52.1(6), 39.9(6), 17.9(6), and -33.4(6)° respectively. The orientation

Table 28

Weighted least-squares mean planes

(a) Distances (Å) of relevant atoms from the mean planes

Atom	d	d/σ	Atom	d	d/σ
Plane 1: C(4)-C(9)			**Plane 2: C(10)-C(15)**		
C(4)	-0.001	0.1	C(10)	0.005	0.5
C(5)	-0.004	0.5	C(11)	0.006	0.0
C(6)	0.012	1.3	C(12)	-0.007	0.1
C(7)	-0.009	1.3	C(13)	-0.007	0.4
C(8)	0.007	0.8	C(14)	0.007	1.2
C(9)	0.000	0.0	C(15)	-0.006	1.1
B	0.070	10.5	B	0.105	18.0
H(5)	0.088	1.6	H(11)	0.062	0.8
H(6)	0.285	6.1	H(12)	0.143	2.5
H(7)	0.116	1.7	H(13)	-0.137	1.7
H(8)	-0.104	1.9	H(14)	0.357	3.7
H(9)	-0.195	1.8	H(15)	0.150	2.5

(b) Equations of planes: $lX + mY + nZ = p$, where X, Y, and Z are orthogonal angstrom coordinates derived as follows:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$$

Plane	l	m	n	p
1	0.1930	-0.0163	-0.9811	0.1760
2	-0.8458	0.2917	-0.4468	-4.2290

The dihedral angle between the planes is 74°.

Table 29

Selected intra- and intermolecular contacts

Intramolecular		Intermolecular*	
Atoms	distance	Atoms	distance
O(1)...H(2A)	2.55(7)	C(3)...C(11)[1]	3.393(9)
O(1)...C(2)	3.100(8)	C(3)...C(12)[1]	3.488(10)
O(1)...C(9)	3.137(7)	O(1)...H(3B)[2]	2.24(6)
O(1)...C(15)	3.013(8)	C(1)...H(3B)[2]	2.69(6)
O(2)...H(2A)	2.26(8)	C(4)...H(3C)[3]	2.67(12)
O(2)...H(3A)	2.26(19)	C(7)...H(2B)[3]	2.63(19)
O(2)...H(5)	2.58(5)	C(9)...H(3C)[3]	2.73(13)
O(2)...C(5)	2.916(8)	H(2C)...H(14)[4]	2.46(11)
O(2)...C(11)	2.932(7)	H(5)...H(8)[5]	2.34(7)
C(1)...C(4)	3.117(9)	H(6)...H(8)[5]	2.39(7)

*Superscripts refer to atoms at positions:

[1] $1/2-x$	$y-1/2$	$1/2+z$		[4] $1-x$	$-y$	$1/2+z$
[2] x	$1+y$	z		[5] x	$y-1$	z
[3] $1/2-x$	$1/2+y$	$z-1/2$				
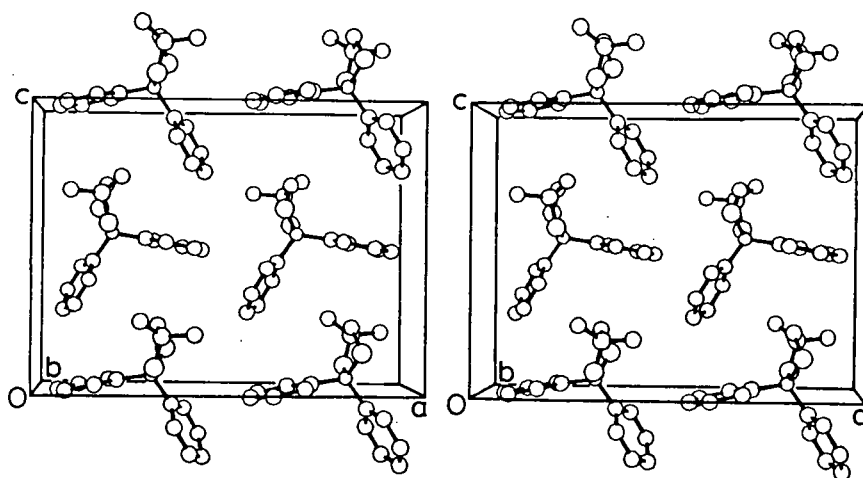
Figure 8

The packing arrangement viewed along <u>b</u>, hydrogen atoms have been omitted for clarity.

of the phenyl groups represents a minimization of intra- and intermolecular steric interactions.

The corrected C-C bond lengths in the phenyl groups range from 1.363 to 1.446 with a mean value of 1.395 Å. There is a significant variation in the individual bond distances, the C(10)-C(17) bond, 1.363 Å, being significantly shorter and the C(8)-C(9), 1.446, and C(12)-C(13), 1.441 Å, bonds significantly longer than the normal value of 1.394 Å (18,51). The means over chemically equivalent groups of bonds (as they are removed from the boron substituent) are 1.384, 1.410, and 1.391 Å. This pattern is different from that observed in the two boroxazolidine structures (Parts 1 and 2) where the bond lengths decrease as they are removed from the boron substituent. The B-C distances are equal within

experimental error and their mean value, 1.632 Å, is longer than in the structures 6a (1.616) and 6b (1.621) but shorter than in the tetraphenyl borate anion (1.631-1.648(8) Å) (19).

The angles in the phenyl rings have a mean value of 120.0°, but the individual values, ranging from 118.0 to 122.5°, show some significant deviations from 120°. The mean angle at the carbon atom carrying the boron group is 118.3° and the other mean values are 121.6, 119.2, and 120.2° for atoms ortho, meta, and para to the boron group. These angular deviations have the same pattern as those in 6a and 6b but the magnitudes of the distortions are one-half as great. These variations have been explained in terms of the electronegativities of the substituent groups (31). The angles at C(4) and C(10), mean 118.3°, carrying the boron substituent indicate that this group is weakly electron releasing.

The overall geometry of the molecule suggests that the formal charges on B and N in 3 are delocalized in a way such that, formally, the B and O(2) carry partial negative charges while N and O(1) carry partial positive charges. This is in accord with the observed pattern of bond distances, particularly the difference between the two B-O distances.

The mean bond angles in the molecule are as expected. There are a number of significant deviations from the mean values resulting from steric and electronic effects. Interior angles in the rings have already been discussed. The C(4)-B-C(10) angle, 112.4(4)°, is significantly smaller than in 6a

and 6b, but is generally as expected. Asymmetry in the packing arrangement appears to be responsible for significant differences between corresponding angle pairs O-B-C and C-N-C.

The geometry involving hydrogen atoms is as follows: mean C(ar)-H, 0.99 $\overset{o}{A}$, mean C($\underline{sp}^3$)-H, 1.14 $\overset{o}{A}$, mean C(ar)-C(ar)-H, 119°, mean R-C($\underline{sp}^3$)-H, 107°, and mean H-C($\underline{sp}^3$)-H, 113°. The distances are long for X-ray data, probably as a result of relatively large thermal motion in the sample.

The crystal structure consists of discrete molecules separated by normal van der Waals distances, the shortest of which are listed in Table 29.

PART 4

CRYSTAL AND MOLECULAR STRUCTURE OF
THE N̲-METHYLDIETHANOLAMINOGALLANE DIMER

INTRODUCTION

Trimethylamine-gallane is known to react with compounds containing active hydrogen to eliminate molecular hydrogen and trimethylamine and form coordinatively unsaturated intermediates which then undergo cyclization to give oligomers whose size depends upon a balance between steric, mechanistic, and valency angle effects (52-54). The present work is part of an extension of this type of reaction involving aminoalcohols where the active hydrogen is attached to oxygen and/or nitrogen atoms. The title compound is derived from N-methyldiethanolamine and trimethylamine-gallane reacted in 1:1 molar ratio. In the title compound four-coordination about the gallium atom can be achieved in monomer units, analogous to similar boron compounds (9,20,Parts 1 and 2), by coordination of two oxygen atoms, one nitrogen atom, and the remaining hydrogen atom, after elimination of two moles of hydrogen and one mole of trimethylamine from the reaction sphere. The metal is indeed coordinated to these atoms but instead of discrete monomer units a novel dimerization through bridging oxygen atoms is realized, to give a distorted trigonal bipyramidal arrangement about each five-coordinate[1] gallium atom (1).

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[1] A preliminary report of the structure of the five-coordinate complex chlorobis-(8-hydroxy-2-methylquinolinato)gallium(III) by K. Dymock and G. J. Palenik, Chem. Comm., 884 (1973) appeared during the preparation of this thesis. The amount of structural information therein does not warrant inclusion of this data in the discussion.
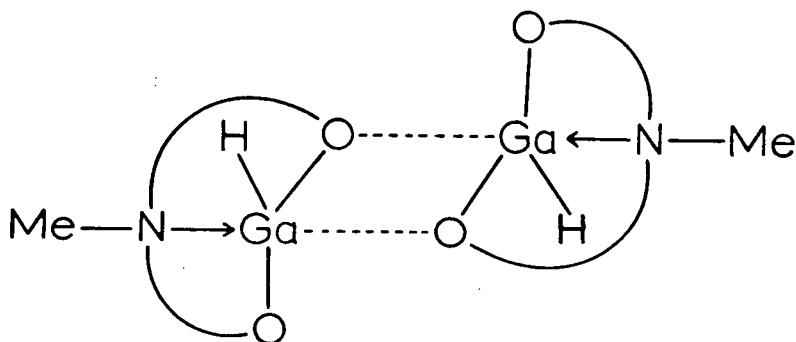
<u>1</u>

EXPERIMENTAL

The <u>N</u>-methyldiethanolaminogallane dimer was prepared by reacting <u>N</u>-methyldiethanolamine (0.226 g; 1.9 mmoles) with trimethylamine - gallane (0.250 g; 1.9 mmoles) in benzene. Hydrogen (84.5 ml; 3.77 mmoles) was evolved at room temperature to leave the product in benzene as a clear solution:

$$MeN(CH_2CH_2OH)_2 + Me_3NGaH_3 \longrightarrow MeN(CH_2CH_2O)_2GaH + 2H_2 + Me_3N$$
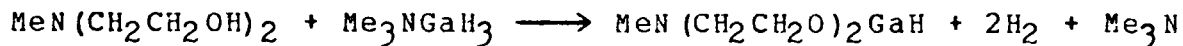
Removal of all volatiles gave a white air-sensitive solid. [Analysis: required for $MeN(CH_2CH_2O)_2GaH$: Ga, 37.1%; hydrol. H, 0.53% found: Ga, 36.9%; hydrol. H, 0.54%.] The compound was redissolved in benzene and the solution cooled to 5° C. Large colorless crystals were deposited from solution after a prolonged period of time. Crystals suitable for X-ray analysis were positioned in capillaries under a nitrogen

atmosphere to avoid the rapid hydrolysis which occurred in contact with moist air. The capillaries were then flame sealed.

The crystal chosen for study was mounted with the [$\bar{2}$ 1 1] vector parallel to the goniostat axis and had dimensions of ca. 0.3 x 0.3 x 0.5 mm. Unit-cell and space group data were obtained from film and diffractometer measurements. The unit-cell parameters were refined by a least-squares treatment of $\sin^2 \theta$ values for 30 reflexions measured on a diffractometer with Cu K_α radiation. Crystal data are:

$C_{10}H_{24}Ga_2N_2O_4$ f.w. = 375.8

Orthorhombic, $\underline{a}$ = 19.112(4), $\underline{b}$ = 9.947(2), $\underline{c}$ = 7.709(2) Å, $\underline{V}$ = 1465.5(5) Å^3, $\underline{Z}$ = 4, $\underline{D}x$ = 1.703(1) g cm^{-3}, $\underline{F}$(000) = 768 (20° C, Cu K_α, λ = 1.5418 Å, μ = 49.7 cm^{-1}). Absent reflexions: $\underline{h}$00, $\underline{h} \neq 2\underline{n}$, 0$\underline{k}$0, $\underline{k} \neq 2\underline{n}$, and 00$\underline{\ell}$, $\underline{\ell} \neq 2\underline{n}$ define uniquely the space group $\underline{P}2_12_12_1$ ($\underline{D}_2^4$, No. 19).

Intensities were measured on a Datex-automated General Electric XRD 6 diffractometer, with a scintillation counter, Cu K_α radiation (nickel filter and pulse height analyser), and a θ-2θ scan at 2° min^{-1} over a range of (1.80 + 0.86 tan θ) degrees in 2θ, with 20 s background counts being measured at each end of the scan. Data were measured to 2θ = 145° (minimum interplanar spacing 0.81 Å). A check reflexion was monitored every 40 reflexions throughout the data collection. The r.m.s. deviation of the intensity of the check reflexion

from its initial value was 2.2% and the final intensity was 1.014 times the initial value. Lorentz and polarization corrections were applied, and the structure amplitudes were derived. No absorption correction was attempted due to the irregularity of the crystal surface (in particular re-entrant angles). Of the 1697 independent reflexions measured, 180 had intensities less than $3\sigma(\underline{I})$ above background where $\sigma^2(\underline{I}) = \underline{S} + \underline{B} + (0.05\underline{S})^2$ with $\underline{S}$ = scan count and $\underline{B}$ = background count, corrected to time of scan. These reflexions were not included in the refinement.

Structure Analysis

The positions of the two gallium atoms were determined from the three-dimensional Patterson function. Three cycles of full-matrix least-squares refinement of the positional and isotropic thermal parameters of the gallium atoms gave $\underline{R}$ 0.27. A difference map revealed the positions of all the C, N, and O atoms. All the non-hydrogen atoms were refined isotropically for three cycles giving $\underline{R}$ 0.096 and then anisotropically for two cycles giving $\underline{R}$ 0.076. A difference map revealed the positions of the gallium H atoms and 12 of the 16 methylene protons. The remaining hydrogen atoms were assigned calculated positions. The hydrogen atoms were included in all subsequent cycles of refinement with isotropic temperature factors. The refinement was concluded after four more cycles with $\underline{R}$ = 0.056 for 1477 reflexions with $\underline{I} > 3\sigma(\underline{I})$.

The absolute configuration of the complex (for the particular crystal used) has been determined through the anomalous scattering of the non-hydrogen atoms. Enantiomorph (A) is represented by the coordinates in Table 31 referred to a right-handed axial system and enantiomorph (B), the mirror image of (A), was generated by changing the x coordinates of (A) to $1-x$. Both enantiomorphs were refined and Hamilton's test (24) applied to the resulting R factor ratios. Enantiomorph (A) was clearly indicated as correct. The results of Hamilton's test are compiled in Table 30.

The scattering factors of ref. 55 were used for the non-hydrogen atoms and those of ref. 13 for the hydrogen atoms. Anomalous scattering factors from ref. 56 were used for Ga, O, N, and C atoms. The weighting scheme: $w = 1$ if $|F_o| \leq 11$; $w = (11/|F_o|)^2$ if $|F_o| > 11$, and $w = 0.49$ for the weak reflexions gave constant average values of $w(F_o-F_c)^2$ over ranges of $|F_o|$ and was employed in the final stages of refinement. On the final cycle of refinement the mean parameter shift was 0.29σ, the largest shifts were 0.85σ for non-hydrogen and 1.70σ for hydrogen atoms, both of which were associated with the C(10) methyl group. The final positional and thermal parameters are given in Tables 31 and 32 respectively. Measured and calculated structure amplitudes are available on request.

THERMAL MOTION AND CORRECTION OF MOLECULAR GEOMETRY

The ellipsoids of thermal motion for the non-hydrogen

Table 30

Results of Hamilton's Test

Parameter compared	Value for enantiomorph			Sig.
	(A)	(B)	(B/A)	level[1]
Conventional $\underline{R}$ (3σ data)	6.126	6.210	1.0137	>99.5
Conventional $\underline{R}$ (all F)	6.491	6.573	1.0125	>99.5
Weighted $\underline{R}$ (3σ data)	8.738	8.878	1.0161	>99.5
Weighted $\underline{R}$ (all F)	9.162	9.232	1.0145	>99.5

[1]This is the % probability that enantiomorph (A) is the correct absolute configuration.

Table 31

Final positional parameters (fractional x 10^4,
Ga x10^5, H x10^3)

with estimated standard deviations in parentheses

Atom	x	y	z
Ga(1)	41623(5)	20988(9)	38421(13)
Ga(2)	40777(5)	27950(8)	76738(12)
O(1)	4292(3)	1238(5)	6085(7)
O(2)	3291(4)	2739(6)	3234(10)
O(3)	4335(3)	3645(5)	5470(8)
O(4)	3170(4)	2235(6)	8000(9)
N(1)	3704(4)	126(7)	3277(10)
N(2)	3662(4)	4807(7)	8153(11)
C(1)	3999(6)	-794(8)	4579(14)
C(2)	4036(6)	-97(8)	6316(13)
C(3)	2961(5)	424(9)	3574(18)
C(4)	2800(5)	1779(9)	2715(16)
C(5)	3837(9)	-343(12)	1516(18)
C(6)	4032(5)	5690(8)	6919(15)
C(7)	4118(6)	4996(8)	5206(13)
C(8)	2928(5)	4611(9)	7696(15)
C(9)	2686(5)	3265(9)	8447(17)
C(10)	3763(7)	5237(11)	9954(16)
H(Ga1)	475(5)	217(9)	282(11)
H(Ga2)	461(4)	268(7)	899(9)
H(1A)	445(5)	-90(10)	430(14)
H(1B)	365(5)	-151(9)	463(12)
H(2A)	426(8)	-81(14)	713(18)
H(2B)	353(5)	5(11)	653(15)
H(3A)	290(6)	34(12)	476(18)
H(3B)	258(6)	-27(10)	312(13)
H(4A)	273(4)	165(8)	141(11)
H(4B)	241(10)	194(17)	304(26)
H(5A)	342(10)	-102(20)	142(29)
H(5B)	380(8)	32(18)	76(22)
H(5C)	426(5)	-41(10)	131(13)
H(6A)	460(6)	566(13)	735(15)
H(6B)	375(7)	641(13)	679(17)
H(7A)	443(7)	548(14)	467(18)
H(7B)	377(7)	490(12)	460(15)
H(8A)	289(5)	434(11)	629(17)
H(8B)	276(11)	516(19)	859(28)
H(9A)	263(6)	318(11)	997(15)
H(9B)	213(6)	290(11)	795(14)
H(10A)	334(8)	598(19)	990(22)
H(10B)	340(9)	453(17)	1086(24)
H(10C)	431(6)	548(12)	1021(15)

Table 32

Final thermal parameters and

their estimated standard deviations

(a) Anisotropic thermal parameters ($\underline{U}_{11}$ x 100 $\overset{\circ}{A}{}^2$)

Atom	$\underline{U}_{11}$	$\underline{U}_{22}$	$\underline{U}_{33}$	$\underline{U}_{12}$	$\underline{U}_{13}$	$\underline{U}_{23}$
Ga(1)	5.47(6)	3.23(5)	4.90(6)	-0.30(4)	0.36(4)	0.20(4)
Ga(2)	5.16(6)	2.86(5)	4.97(6)	0.08(4)	-0.27(4)	0.14(4)
O(1)	5.8(3)	3.1(2)	4.7(3)	0.5(2)	0.0(3)	0.2(2)
O(2)	7.5(4)	2.9(3)	8.1(4)	-0.1(3)	-1.9(3)	1.4(3)
O(3)	6.3(3)	2.8(2)	5.1(3)	-0.9(2)	0.1(3)	0.2(2)
O(4)	6.5(3)	3.1(3)	7.5(4)	-0.1(3)	1.0(3)	0.4(3)
N(1)	5.7(4)	3.1(3)	5.5(4)	-0.1(3)	-0.5(3)	0.3(3)
N(2)	5.6(4)	2.9(3)	6.3(4)	0.1(3)	0.5(3)	0.5(3)
C(1)	6.5(6)	3.2(4)	6.5(5)	0.7(4)	-0.9(5)	-0.1(4)
C(2)	6.8(6)	3.6(4)	5.3(5)	-0.1(4)	-0.6(4)	0.6(4)
C(3)	5.8(5)	3.7(4)	9.0(8)	-0.1(4)	-0.5(5)	0.7(5)
C(4)	5.9(5)	4.2(4)	8.3(7)	-0.1(4)	-1.8(5)	1.1(4)
C(5)	9.3(10)	4.9(5)	7.1(7)	-0.4(6)	0.6(7)	-0.8(5)
C(6)	6.3(6)	2.7(4)	7.6(6)	-0.5(4)	0.7(5)	0.0(4)
C(7)	6.3(5)	3.7(4)	6.0(5)	-0.7(4)	1.0(5)	1.0(4)
C(8)	5.8(5)	3.5(4)	7.1(6)	-0.5(3)	0.5(4)	0.9(4)
C(9)	6.0(5)	3.8(4)	9.0(7)	0.6(4)	1.8(5)	1.4(4)
C(10)	10.1(9)	4.2(5)	6.6(6)	0.5(5)	-0.4(6)	-1.4(5)

(b) Isotropic thermal parameters

Atom	$\underline{B}(\overset{\circ}{A}{}^2)$	Atom	$\underline{B}(\overset{\circ}{A}{}^2)$
H(Ga1)	3.9(19)	H(Ga2)	2.3(13)
H(1A)	4.3(21)	H(6A)	7.0(29)
H(1B)	3.0(17)	H(6B)	5.4(28)
H(2A)	8.8(30)	H(7A)	6.5(29)
H(2B)	3.6(21)	H(7B)	4.3(28)
H(3A)	4.8(27)	H(8A)	2.6(23)
H(3B)	4.0(20)	H(8B)	11.9(52)
H(4A)	1.7(12)	H(9A)	3.0(24)
H(4B)	12.3(51)	H(9B)	10.2(23)
H(5A)	17.4(50)	H(10A)	13.7(44)
H(5B)	8.0(40)	H(10B)	4.7(47)
H(5C)	2.1(18)	H(10C)	5.2(24)
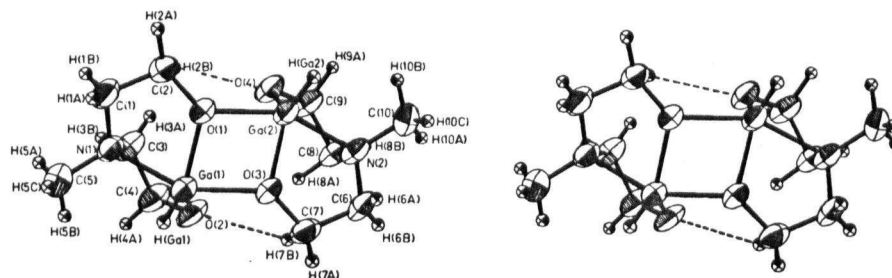
Figure 9

A stereo view of the molecule along the
C_2 axis showing the atom numbering and
50% probability thermal ellipsoids for
the non-hydrogen atoms. Broken lines show
possible C-H...O hydrogen bonds.

atoms are shown in Figure 9. The thermal motion has been
analysed in terms of the rigid-body modes of translation ($\underline{T}$),
libration ($\underline{L}$), and screw ($\underline{S}$) motion using the computer
program MGTLS (14). The r.m.s. standard deviation in the
temperature factors $\underline{U}_{11}$ is 0.0042 $\mathring{A}^2$ which indicates that the
thermal motion of the molecule as a whole (r.m.s. $\Delta \underline{U}_{11}$ =
0.0054 $\mathring{A}^2$) is adequately described by the rigid-body
parameters in Table 33. The indicated modes of motion are
physically reasonable; the translational and librational
motions are both somewhat anisotropic. The orientation of the
principal axes of $\underline{L}$ is nearly coincident with that of the
principal axes of inertia, the largest librational motion
occurring about the least axis of inertia.

Table 33

Rigid-body thermal parameters[1]

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all non-hydrogen atoms

$\underline{L}$ (x 10 deg²)

$$\begin{bmatrix} 49\,(9) & -14\,(9) & -4\,(8) \\ & 157\,(21) & 46\,(13) \\ & & 69\,(15) \end{bmatrix}$$

Principal axes of $\underline{L}$

r.m.s. Amplitude	Direction cosines (x10³)		
4.2°	-108	914	392
2.2	-506	288	-813
2.2	-856	-286	430

Principal axes of reduced $\underline{T}$

r.m.s. Amplitude	Direction cosines (x10³)		
0.23Å	-1	-268	-963
0.22	997	-73	20
0.16	-76	-960	267

Displacement of axes from intersecting (Å)

Parallel to $\underline{L}_1$	0.65
Parallel to $\underline{L}_2$	-0.53
Parallel to $\underline{L}_3$	-0.32

Effective screw translations (Å)

Parallel to $\underline{L}_1$	0.036
Parallel to $\underline{L}_2$	-0.039
Parallel to $\underline{L}_3$	-0.031

Fractional coordinates of unique origin (x10⁴)

$\underline{x}$	3862
$\underline{y}$	2358
$\underline{z}$	5740

Fractional coordinates of centre of gravity (x10⁴)

$\underline{x}$	3818
$\underline{y}$	2462
$\underline{z}$	5721

r.m.s. $\Delta \underline{U}_{11}$ (Å²)   0.0054

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[1]Axes of reference are orthogonal angstrom axes. E.s.d.'s of components of $\underline{L}$ are given in parentheses in units of the last places shown.

The appropriate bond distances and angles have been corrected for libration (15,16), using shape parameters q^2 of 0.08 for all the atoms involved, and appear in Tables 34 and 35 respectively.

RESULTS AND DISCUSSION

The X-ray analysis has provided the first known crystallographic example of pentacoordinate gallium as well as the first reported Ga-H distances. The numbering scheme is shown in Figure 9, in which the molecule is viewed along its approximate C_2 axis. Figure 10 shows the coordination about the gallium atoms and Figures 11 and 12 show the crystal structure viewed along c and b respectively. Ga-N and Ga-O bond distances in related four and six-coordinate structures are compiled in Table 36. Some weighted least-squares mean planes through the molecule are given in Table 37 and the dihedral angles in the five fused rings of the molecule in Table 38. Selected inter- and intramolecular contacts are listed in Table 39.

The molecule has C_2 symmetry within the limits of experimental error. The bond distances, valence angles, and dihedral angles averaged assuming C_2 symmetry also appear in the appropriate tables and will be employed in the discussion of the molecular geometry. The molecule exhibits, in part, the structure expected for the monomeric boron analogue (on the basis of the structures of triethanolamine borate (20), B,B-diphenylboroxazolidine (Part 1), and B,B-bis(p-fluorophenyl) boroxazolidine (Part 2), and supporting

Table 34

Bond lengths (Å) with estimated

standard deviations in parentheses

(a) Non-hydrogen atoms

Atoms	uncorr.	corr.	Atoms	uncorr.	corr.	mean*
Ga(1)-O(1)	1.945(6)	1.952	Ga(2)-O(3)	1.960(6)	1.967	1.960(8)
Ga(1)-O(2)	1.843(7)	1.848	Ga(2)-O(4)	1.839(7)	1.845	1.847(2)
Ga(1)-O(3)	2.012(6)	2.016	Ga(2)-O(1)	2.016(6)	2.019	2.018(2)
Ga(1)-N(1)	2.193(7)	2.196	Ga(2)-N(2)	2.184(7)	2.187	2.192(5)
O(1)-C(2)	1.427(10)	1.429	O(3)-C(7)	1.422(10)	1.424	1.427(3)
O(2)-C(4)	1.398(11)	1.399	O(4)-C(9)	1.422(11)	1.424	1.412(13)
N(1)-C(1)	1.471(12)	1.475	N(2)-C(6)	1.475(12)	1.479	1.477(2)
N(1)-C(3)	1.468(13)	1.471	N(2)-C(8)	1.460(12)	1.464	1.468(4)
N(1)-C(5)	1.458(15)	1.460	N(2)-C(10)	1.466(14)	1.468	1.464(4)
C(1)-C(2)	1.510(14)	1.512	C(6)-C(7)	1.499(14)	1.501	1.507(6)
C(3)-C(4)	1.533(13)	1.535	C(8)-C(9)	1.531(12)	1.533	1.534(1)

(b) Bonds involving hydrogen atoms

Atoms	distance	Atoms	distance
Ga(1)-H(Ga1)	1.37(8)	Ga(2)-H(Ga2)	1.45(7)
C(1)-H(1A)	0.90(10)	C(6)-H(6A)	1.14(12)
C(1)-H(1B)	0.98(9)	C(6)-H(6B)	0.90(13)
C(2)-H(2A)	1.04(14)	C(7)-H(7A)	0.87(14)
C(2)-H(2B)	0.99(10)	C(7)-H(7B)	0.82(12)
C(3)-H(3A)	0.93(14)	C(8)-H(8A)	1.12(13)
C(3)-H(3B)	1.06(11)	C(8)-H(8B)	0.94(20)
C(4)-H(4A)	1.02(8)	C(9)-H(9A)	1.18(11)
C(4)-H(4B)	0.81(19)	C(9)-H(9B)	1.20(11)
C(5)-H(5A)	1.05(20)	C(10)-H(10A)	1.10(18)
C(5)-H(5B)	0.89(18)	C(10)-H(10B)	1.21(16)
C(5)-H(5C)	0.83(9)	C(10)-H(10C)	1.09(12)

*Average of bonds related by the C_2 axis, number in parentheses is r.m.s. deviation from the mean.

Table 35

Bond angles (deg) with estimated

standard deviations in parentheses

(a) Non-hydrogen atoms

Atoms	uncorr.	corr.	Atoms	uncorr.	corr.	mean*
O(1)-Ga(1)-O(2)	119.5(3)	119.5	O(3)-Ga(2)-O(4)	119.1(3)	119.1	119.3(2)
O(1)-Ga(1)-O(3)	76.2(2)	76.2	O(3)-Ga(2)-O(1)	75.8(2)	75.7	76.0(3)
O(1)-Ga(1)-N(1)	80.4(3)	80.4	O(3)-Ga(2)-N(2)	80.9(3)	80.9	80.7(3)
O(2)-Ga(1)-O(3)	92.5(3)	92.5	O(4)-Ga(2)-O(1)	92.4(3)	92.4	92.5(1)
O(2)-Ga(1)-N(1)	84.1(3)	84.0	O(4)-Ga(2)-N(2)	84.9(3)	84.9	84.5(5)
O(3)-Ga(1)-N(1)	150.9(3)	150.8	O(1)-Ga(2)-N(2)	151.6(3)	151.6	151.2(4)
Ga(1)-O(1)-Ga(2)	100.1(2)	100.2	Ga(2)-O(3)-Ga(1)	99.7(2)	99.8	100.0(2)
Ga(1)-O(1)-C(2)	118.5(5)	118.5	Ga(2)-O(3)-C(7)	117.3(6)	117.3	117.9(6)
Ga(2)-O(1)-C(2)	124.8(5)	124.7	Ga(1)-O(3)-C(7)	125.8(6)	125.7	125.2(5)
Ga(1)-O(2)-C(4)	116.4(5)	116.4	Ga(2)-O(4)-C(9)	115.4(5)	115.3	115.9(6)
Ga(1)-N(1)-C(1)	105.6(5)	105.5	Ga(2)-N(2)-C(6)	105.2(5)	105.2	105.4(2)
Ga(1)-N(1)-C(3)	100.1(5)	100.1	Ga(2)-N(2)-C(8)	100.7(5)	100.8	100.5(4)
Ga(1)-N(1)-C(5)	113.7(7)	113.6	Ga(2)-N(2)-C(10)	112.3(6)	112.3	113.0(7)
C(1)-N(1)-C(3)	113.0(8)	112.9	C(6)-N(2)-C(8)	112.6(8)	112.6	112.8(2)
C(1)-N(1)-C(5)	111.6(8)	111.7	C(6)-N(2)-C(10)	112.0(8)	112.0	111.9(2)
C(3)-N(1)-C(5)	112.2(9)	112.3	C(8)-N(2)-C(10)	113.2(9)	113.2	112.8(5)
N(1)-C(1)-C(2)	109.7(7)	109.8	N(2)-C(6)-C(7)	110.2(7)	110.3	110.1(3)
N(1)-C(3)-C(4)	107.7(8)	107.7	N(2)-C(8)-C(9)	108.4(8)	108.4	108.1(4)
C(1)-C(2)-O(1)	109.5(7)	109.4	C(6)-C(7)-O(3)	109.9(8)	109.9	109.7(3)
C(3)-C(4)-O(2)	110.0(8)	110.1	C(8)-C(9)-O(4)	110.0(8)	110.0	110.1(1)

(b) Angles involving hydrogen atoms

Atoms	value	Atoms	value
O(1)-Ga(1)-H(Ga1)	115(4)	O(3)-Ga(2)-H(Ga2)	118(3)
O(2)-Ga(1)-H(Ga1)	125(4)	O(4)-Ga(2)-H(Ga2)	123(3)
O(3)-Ga(1)-H(Ga1)	101(4)	O(1)-Ga(2)-H(Ga2)	103(3)
N(1)-Ga(1)-H(Ga1)	105(4)	N(2)-Ga(2)-H(Ga2)	102(3)
N(1)-C(1)-H(1A)	106(7)	N(2)-C(6)-H(6A)	105(6)
N(1)-C(1)-H(1B)	102(5)	N(2)-C(6)-H(6B)	104(8)
C(2)-C(1)-H(1A)	103(7)	C(7)-C(6)-H(6A)	98(6)
C(2)-C(1)-H(1B)	109(5)	C(7)-C(6)-H(6B)	109(8)
H(1A)-C(1)-H(1B)	126(8)	H(6A)-C(6)-H(6B)	129(10)
O(1)-C(2)-H(2A)	125(8)	O(3)-C(7)-H(7A)	113(9)
O(1)-C(2)-H(2B)	103(6)	O(3)-C(7)-H(7B)	102(9)
C(1)-C(2)-H(2A)	104(7)	C(6)-C(7)-H(7A)	104(9)
C(1)-C(2)-H(2B)	100(7)	C(6)-C(7)-H(7B)	118(8)
H(2A)-C(2)-H(2B)	113(11)	H(7A)-C(7)-H(7B)	110(12)
N(1)-C(3)-H(3A)	105(7)	N(2)-C(8)-H(8A)	109(5)
N(1)-C(3)-H(3B)	118(6)	N(2)-C(8)-H(8B)	94(12)
C(4)-C(3)-H(3A)	119(8)	C(9)-C(8)-H(8A)	98(6)
C(4)-C(3)-H(3B)	107(5)	C(9)-C(8)-H(8B)	98(12)
H(3A)-C(3)-H(3B)	101(9)	H(8A)-C(8)-H(8B)	146(15)
O(2)-C(4)-H(4A)	117(4)	O(4)-C(9)-H(9A)	104(6)
O(2)-C(4)-H(4B)	114(13)	O(4)-C(9)-H(9B)	107(5)
C(3)-C(4)-H(4A)	110(4)	C(8)-C(9)-H(9A)	118(6)
C(3)-C(4)-H(4B)	103(13)	C(8)-C(9)-H(9B)	115(5)
H(4A)-C(4)-H(4B)	103(15)	H(9A)-C(9)-H(9B)	103(8)
N(1)-C(5)-H(5A)	98(12)	N(2)-C(10)-H(10A)	94(9)
N(1)-C(5)-H(5B)	111(10)	N(2)-C(10)-H(10B)	107(9)
N(1)-C(5)-H(5C)	112(7)	N(2)-C(10)-H(10C)	111(6)
H(5A)-C(5)-H(5B)	111(14)	H(10A)-C(10)-H(10B)	89(11)
H(5A)-C(5)-H(5C)	133(13)	H(10A)-C(10)-H(10C)	124(11)
H(5B)-C(5)-H(5C)	91(12)	H(10B)-C(10)-H(10C)	125(10)

*mean of corrected angles related by the C_2 axis, number in parentheses is the r.m.s. deviation from the mean.

chemical evidence (9)) in that the $MeN(CH_2CH_2O)_2$ acts as a tridentate ligand, the nitrogen and two oxygen atoms all being coordinated to the same gallium atom. Here the similarity to the boron compounds ends as dimerization occurs through bridging oxygen atoms, creating a four-membered Ga_2O_2 ring which results in the formation of a molecule possessing a system of five fused rings. A polymeric structure might be expected of the compound produced by the reaction of trimethylamine-gallane and N-methyldiethanolamine even though gallium has a high tendency to form four-membered rings with oxygen (57,58). Thus polymerization through nitrogen or oxygen atoms (ie. the $MeN(CH_2CH_2O)_2$ acting as a bridging ligand) to form large heterocycles with tetrahedral coordination about the gallium atoms was originally suspected.

The resulting structure contains pentacoordinate gallium atoms with distorted trigonal bipyramidal geometry. The nitrogen and two oxygen atoms of each $MeN(CH_2CH_2O)_2$ ligand occupy respectively an axial and two equatorial positions about the associated gallium atom. One of the oxygen atoms bridges the two gallium atoms, occupying an axial position of the second gallium atom. The remaining equatorial site is occupied by the hydrogen atom (see Fig. 10).

The axial Ga-N distance of 2.192 (5) $\overset{\circ}{A}$ is longer than the observed distances for tetrahedral (mean 1.97 $\overset{\circ}{A}$) and for octahedral gallium (mean 2.12 $\overset{\circ}{A}$) shown in Table 36. The distance compares well with a sterically similar bond in
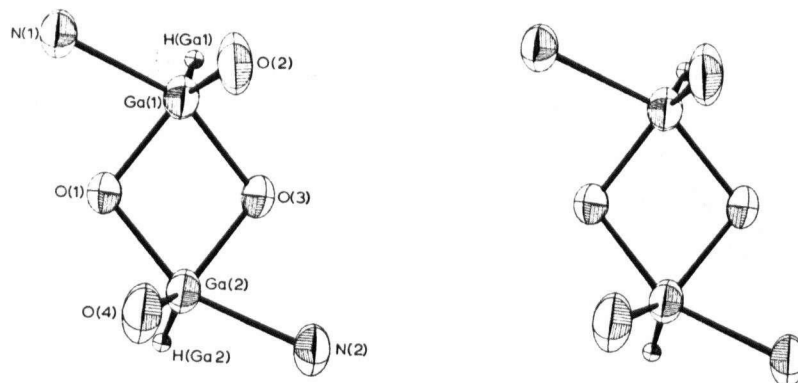
Figure 10

A view of the coordination about the gallium atoms.

octahedral GaH(EDTA).H_2O (59) of 2.182(5) Å and the axial Al-N distance of 2.18 Å in $AlH_3(NMe_3)_2$ (60). The bond nevertheless appears to be be weaker than a normal single bond as a result cf steric strain as in the related aminoalcohol boron compounds (20,Parts 1 and 2). The three types of Ga-O bonds are all significantly different. The equatorial non-bridging distance is 1.847(2) Å and for the bridging oxygen the equatorial distance is 1.960(8) and the axial is 2.018(2) Å. The equatorial bonds involve sp^2 hybrids at the gallium atoms which reduces the covalent radius of gallium to 1.21 Å for these bonds. The expected equatorial Ga-O distance is then about 1.87 Å. The mean Ga-O distances in related four-coordinate and octahedral complexes are 1.96 and 1.959 Å respectively. In this structure the 1.847 Å 'terminal' Ga-O distance corresponds to a strong bond while

Table 36

Comparison of Ga-O and Ga-N bond distances

Compound	Ga Coord. no.	Ga-O	Ga-N	ref.
GaN	4		1.94	62
$(H_2GaNCH_2CH_2)_3$	4		1.97	53
$[D_2Ga(N_2C_3H_3)]_2$	4		1.980	54
$[(CH_3)_2GaOH]_4$	4	1.94,1.98		63
$(CH_3)_3NGaH_3$	4		1.97	64
$[CH_3N(CH_2CH_2O)_2GaH]_2$	5	1.843-2.019	2.187,2.196	*
$[Ga_2(OH)_2Cl_2(C_{14}H_{17}N_3)_2]Cl_2.H_2O$	6	1.908,2.017	2.083-2.132	58
$GaH(EDTA).H_2O$	6	1.924-1.996	2.097,2.182	59
$[GaCl_2(bipy)_2]^+[GaCl_4]^-$	6		2.097,2.105	65
$GaCl_3(terpy)$	6		2.034-2.115	66

*this work

the bridge bonds, 1.960 and 2.018 Å, seem to be of nearly equal strength considering that one is axial and the other equatorial and both these distances are within the range of previously reported Ga-O bond lengths (see Table 36). Using an effective radius of 0.23 Å for hydrogen (61), the expected Ga-H bond length is 1.44 Å in good agreement with the mean Ga-H distance of 1.41(4) Å.

The distortion of the trigonal bipyramid occurs as a deformation of the angle between the axial groups from the ideal 180° to 151.2(4)°. The equatorial GaOOH groups are both planar within experimental error (see Table 37) and the mean O-Ga-O, 119.3(2)°, and O-Ga-H angles, 120.3°, are close to the expected 120°. The equatorial-Ga-axial angles range from 76° (in the four-membered ring) to 104° (mean N-Ga-H), each 14° from the ideal 90°. The angular distortions are a result of the steric constraints inherent in the fused ring system.

The four-membered Ga_2O_2 ring is non-planar with all intra-annular dihedral angles equal within experimental error, the mean value being 21.6°. Angles in the ring are 76.0(3) at Ga and 100.0(2)° at O. The ring is different from the planar centrosymmetric Ga_2O_2 ring in the octahedral complex $[Ga_2(OH)_2Cl_2(C_{14}H_{17}N_3)_2]Cl_2 \cdot H_2O$ (16) in which there is one strong and one weak Ga-O bond (1.908 and 2.017 Å).

The difference between the 'terminal' and 'bridging' oxygen atoms is carried into the five-membered GaOCCN rings which have distinct geometries which may be ascribed to steric and electronic differences between the two classes of

Table 37

Intra-annular torsion angles (deg)

(a) Five membered rings

Bond	obs.	Bond	obs.	mean	calc.
Ga(1)-O(1)	2.1(5)	Ga(2)-O(3)	3.4(5)	2.8(7)	5.0
O(1)-C(2)	-25.0(8)	O(3)-C(7)	-26.4(8)	-25.7(7)	-29.8
C(2)-C(1)	43.3(8)	C(7)-C(6)	44.1(8)	43.7(4)	43.0
C(1)-N(1)	-39.8(7)	C(6)-N(2)	-39.2(7)	-39.5(3)	-40.0
N(1)-Ga(1)	21.4(5)	N(2)-Ga(2)	20.1(5)	20.8(7)	21.8

Bond	obs.	Bond	obs.	mean	calc.
Ga(1)-O(2)	1.2(5)	Ga(2)-O(4)	2.7(5)	2.0(8)	1.3
O(2)-C(4)	-27.5(8)	O(4)-C(9)	-28.3(8)	-27.9(4)	-27.1
C(4)-C(3)	50.3(9)	C(9)-C(8)	49.6(9)	50.0(4)	42.3
C(3)-N(1)	-44.1(7)	C(8)-N(2)	-42.6(7)	-43.4(8)	-41.6
N(1)-Ga(1)	25.3(6)	N(2)-Ga(2)	23.5(5)	24.4(11)	25.0

(b) Four-membered ring

Bond	obs.
Ga(1)-O(1)	-21.3(2)
O(1)-Ga(2)	22.0(2)
Ga(2)-O(3)	-21.2(2)
O(3)-Ga(1)	21.9(2)

Table 38

Weighted least-squares mean planes

(a) Distances (Å) of relevant atoms from the mean planes

Atom	d	d/σ	Atom	d	d/σ
1: Ga(1), O(1), O(2), H(Ga1)			2: Ga(2), O(3), O(4), H(Ga2)		
Ga(1)	0.000	0.0	Ga(2)	0.000	0.0
O(1)	0.000	0.0	O(3)	0.000	0.0
O(2)	0.000	0.0	O(4)	0.000	0.0
H(Ga1)	0.005	0.1	H(Ga2)	0.042	0.6

(b) Equations of planes: $\ell X + m Y + n Z = p$, where X, Y, and Z are orthogonal angstrom coordinates derived as follows:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$$

Plane	ℓ	m	n	p
1	0.2240	0.8857	0.4066	4.8355
2	-0.2331	0.8959	0.3783	2.9117

The angle between the plane normals is 26.5°

rings. The mean dihedral angles in each type of ring are compared with those obtained from energy minimization calculations (17) in Table 38. The conformational differences between the two types of five-membered rings are small yet the rings with the 'bridging' oxygen atoms (A rings) have a conformation which is closest to that calculated for $\omega_1 = 5.0°$ while those containing the 'terminal' oxygens (B rings) have a conformation nearest to that calculated for $\omega_1 = 25.0°$. Both ring types show some strain relative to the minimum energy conformations but the B rings show higher strain (4.0° r.m.s. deviation between $\omega_{obs.}$ and $\omega_{calc.}$ compared to 2.4° for the A rings), this occurring primarily in the twist about the C-C bonds.

Bond angles in the A rings range from 80.7(3)° at Ga to 117.9(6)° at O and in the B rings from 84.5(5)° at Ga to 115.9(6)° at O with mean values of 104.8 and 103.8° in A and B rings respectively compared to the calculated value of 104.2° (17) and observed values in BOCCN rings of 104.8° (Part 1) and 104.9° (Part 2). The C-O, C-C, and C-N distances are 1.427(3), 1.507(6), and 1.477(2) Å in the A rings and 1.412(13), 1.534(1), and 1.468(4) Å in the B rings. The differences in the bond lengths and angles in the two types of rings are a result of steric and electronic differences between the corresponding atoms in the ring, and to some extent are indicative of the charge distribution in the molecule. The mean C-O, C-C, and C-N distances in the two structures with BOCCN rings (Parts 1 and 2) are 1.416(3), 1.500(6), and 1.488(3) Å. The mean N-C(methyl) distance of

1.464(4) $\overset{o}{A}$ in the present structure is as expected. The mean angle at nitrogen is 109.4° but the individual angles all differ significantly from the mean and range from 100.5(4)° for Ga-N-C(B ring) to 113.0(7)° for Ga-N-C(methyl). The angle at N between the A and B rings is 112.8(2)°. The distortion of the nitrogen tetrahedron results from steric constraints imposed by the fused-ring system.

The mean C-H distance of 1.00(13) $\overset{o}{A}$ is as expected for X-ray data (61). All angles involving hydrogen atoms (R-C-H, R = N,O,C,H) are within three standard deviations of the mean value of 109°.
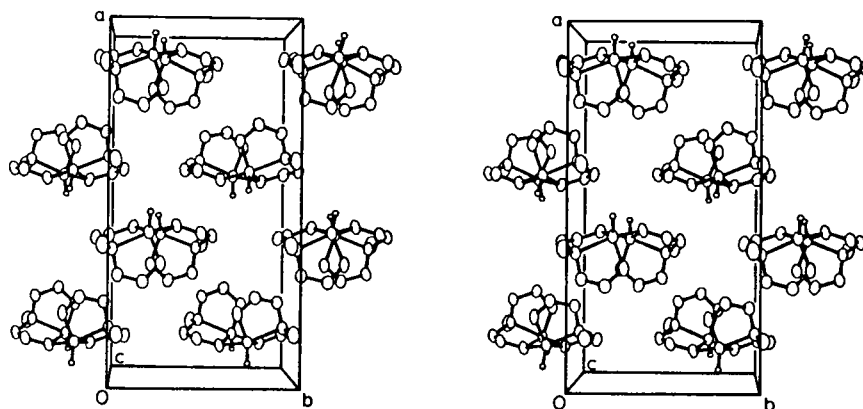
Figure 11

The packing arrangement viewed along $\underline{c}$.

The crystal structure consists of discrete [CH$_3$N(CH$_2$CH$_2$O)$_2$GaH]$_2$ molecules which are separated by normal
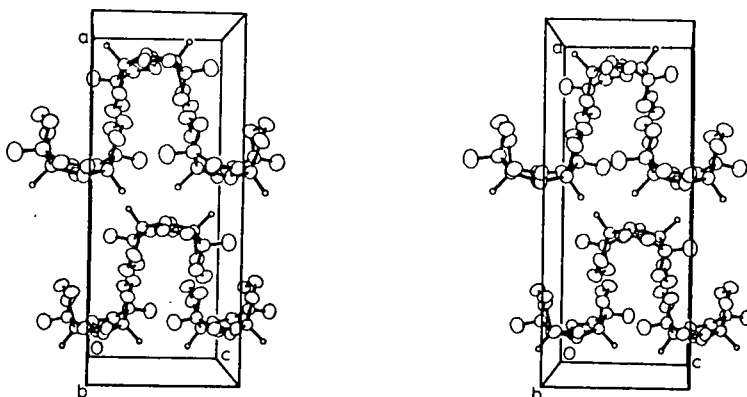
Figure 12

The packing arrangement viewed along b.

van der Waals distances, the shortest of which are listed in Table 39, except for one C-H...O interaction (C...O = 3.44(1) Å) which may correspond to a weak hydrogen bond. There are also two possible intramolecular C-H...O hydrogen bonds present (related by the two-fold rotation axis) which are indicated by broken lines in Figure 9. The geometrical data for these C-H...O interactions are given in Table 39. The asymmetry introduced by the intermolecular O(4)...H(3B)-C(3) interaction is a reasonable explanation for the difference between the C(4)-O(2), 1.399, and C(9)-O(4), 1.424 Å, bond distances (which represents the largest deviation from C_2 symmetry in the molecule). The non-bonded contacts in the gallium coordination spheres and other intramolecular non-bonded contacts which correspond to steric interactions within the molecule are also listed in Table 39.

Table 39

(a) Selected intra- and intermolecular contacts

Intramolecular		Intermolecular*	
Atoms	distance	Atoms	distance
C(2)...C(3)	2.99(2)	O(4)...C(3) [1]	3.44(1)
C(7)...C(8)	3.00(1)	Ga(1)...H(10C) [2]	3.41(12)
C(4)...C(5)	3.04(2)	Ga(2)...H(6A) [2]	3.30(12)
C(9)...C(10)	3.07(2)	Ga(2)...H(5B) [3]	3.46(18)
C(2)...H(3A)	2.52(12)	Ga(2)...H(2A) [4]	3.48(15)
C(7)...H(8A)	2.58(11)	O(1)...H(6A) [2]	2.50(12)
C(3)...H(2B)	2.55(11)	O(2)...H(10B) [5]	2.57(17)
C(9)...H(10B)	2.68(18)	C(4)...H(9A) [5]	2.56(11)
H(2B)...H(3A)	1.84(17)	C(9)...H(4A) [3]	2.79(8)
H(7B)...H(8A)	2.20(16)	H(1B)...H(9B) [1]	2.40(14)
H(9A)...H(10B)	2.10(19)	H(4A)...H(9A) [5]	1.90(15)

(b) Gallium coordination sphere

Atoms	distance	Atoms	distance
Ga(1)...Ga(2)	3.038(2)	O(1)...O(3)	2.442(8)
O(1)...O(2)	3.273(8)	O(3)...O(4)	3.275(9)
O(1)...N(1)	2.678(10)	O(3)...N(2)	2.695(10)
O(2)...O(3)	2.787(9)	O(4)...O(1)	2.785(9)
O(2)...N(1)	2.716(9)	O(4)...N(2)	2.728(9)
O(1)...H(Ga1)	2.82(8)	O(3)...H(Ga2)	2.92(7)
O(2)...H(Ga1)	2.86(9)	O(4)...H(Ga2)	2.90(8)
O(3)...H(Ga1)	2.63(8)	O(1)...H(Ga2)	2.73(7)
N(1)...H(Ga1)	2.87(9)	N(2)...H(Ga2)	2.86(7)

(c) Possible C-H...O hydrogen bonds

D-H...A	H...A	D...A	∠DHA	∠XAH
C(7)-H(7B)...O(2)	2.56(12)	3.14(1)	129(10)	82(3),158(3)
C(2)-H(2B)...O(4)	2.55(11)	3.13(1)	118(8)	88(3),154(2)
C(3)-H(3B)...O(4) [1]	2.43(11)	3.44(1)	160(8)	144(3),101(3)

The H...O...H angle at O(4) is 59(3)°

*Superscripts refer to atoms at positions:

[1] 1/2-x	-y	z-1/2	
[2] 1-x	y-1/2	3/2-z	
[3] x	y	1+z	
[4] 1-x	1/2+y	3/2-z	
[5] x	y	z-1	

The infrared spectrum of the title compound in benzene solution showed a very strong Ga-H stretching absorption at 1900 cm^{-1} with a weak shoulder at 1810 cm^{-1}. A medium intensity band at 770 cm^{-1} is assigned to the Ga-H wagging mode. The low frequency spectrum displayed a number of absorptions attributable to 'Ga-O', 'Ga-N' and ring modes (615 sh, 595 vs, 540 vs, 510 vs, 420 s, 390 s, 380 sh) but no assignment of this part of the spectrum is attempted at this time.

Coates and Hayter (57), by chemical tests, postulated that dimerization in [Me$_2$NCH$_2$CH$_2$OGaMe$_2$]$_2$ probably occurs via a four-membered Ga$_2$O$_2$ ring leaving the gallium atoms four-coordinate and the normally stronger nitrogen donor atoms not utilized in coordinate-type bonding. It is tempting, as a result of the present study, to postulate that in the above dimer five-coordinate gallium atoms might again be featured, the bonding about the metal atoms again involving both nitrogen and oxygen atoms to give a fused-ring system. This possibility is under study for the analogous gallane dimer, [Me$_2$NCH$_2$CH$_2$OGaH$_2$]$_2$.

PART 5

CRYSTAL AND MOLECULAR STRUCTURE OF

(PENTAHAPTOCYCLOPENTADIENYL) HYDRIDOMOLYBDENUM-μ-

DIMETHYLALUMINUM-μ-[METHYLALUMINUM-DI-(μ-PENTAHAPTO

(MONOHAPTO) CYCLOPENTADIENYL) DIMETHYLALUMINUM] (PENTAHAPTO

CYCLOPENTADIENYL) HYDRIDOMOLYBDENUM

INTRODUCTION

An earlier report (67) indicated that slow decomposition of the adduct $Cp_2MoH_2.AlMe_3$ occurs in benzene solution at room temperature. Methane is liberated and eventually a solid is deposited from solution. From one such solution a small amount of crystalline material was produced suitable for X-ray analysis and an investigation was carried out to determine the extent of the expected Mo-Al network in the crystals. The novel[1] structure which resulted (shown in Fig. 13) contained two molybdenum and three aluminum atoms per molecular unit.

EXPERIMENTAL

The small amount of crystalline material deposited as a result of the slow methane elimination from benzene solutions of the parent compound, $Cp_2MoH_2.AlMe_3$, was sufficient only for the crystal structure investigation and consequently no chemical analyses are reported. The molecular formula given in the title was derived from the experimental X-ray data collected on the sample.

The air-sensitive crystals were mounted in glass

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[1] During the preparation of this thesis a preliminary report of this structure by Dr. C. K. Prout and co-workers appeared in Chem. Comm., 426 (1973). Correspondence with Dr. Prout, who will in the future publish an account on both this structure and that of the symmetric complex $[(C_5H_4)_4MoH]_2Al_4Me_6$, is acknowledged.

capillary tubes under a nitrogen atmosphere and subsequently sealed off. An irregularly shaped crystal with dimensions of ca. 0.15 x 0.15 x 0.15 mm was mounted with the [0 1 1] vector parallel to the goniostat axis. Unit-cell and space group data were obtained from film and diffractometer measurements. The unit-cell parameters were refined by a least-squares treatment of $\sin^2 \theta$ values for 30 reflexions measured on a diffractometer with Mo K_α radiation. Crystal data are:

$C_{25}H_{35}Al_3Mo_2$ f.w. = 608.4

Orthorhombic, $\underline{a} = 19.398(4)$, $\underline{b} = 14.438(9)$, $\underline{c} = 9.035(2)$ Å, $\underline{V} = 2531(2)$ Å^3, $\underline{Z} = 4$, $\underline{Dx} = 1.597(1)$ g cm^{-3}, $\underline{F}(000) = 1232$ (20° C, Mo K_α, $\lambda = 0.71069$ Å, $\mu = 10.9$ cm^{-1}). Absent reflexions: $\underline{h}00$, $\underline{h} \neq 2\underline{n}$, $0\underline{k}0$, $\underline{k} \neq 2\underline{n}$, and $00\underline{l}$, $\underline{l} \neq 2\underline{n}$ define uniquely the space group $\underline{P}2_1 2_1 2_1$ ($\underline{D}_2^4$, No. 19).

Intensities were measured on a Datex-automated General Electric XRD 6 diffractometer, with a scintillation counter, Mo K_α radiation (zirconium filter and pulse height analyser), and a θ-2θ scan at 2° min^{-1} over a range of (1.80 + 0.86 tan θ) degrees in 2θ, with 20 s background counts being measured at each end of the scan. Data were measured to $2\theta = 45°$ (minimum interplanar spacing 0.93 Å). Later data for $\underline{l} = 0$ to 7 were collected between $2\theta = 45$ and 50° (minimum interplanar spacing 0.84 Å). Data collection in the $2\theta = 45$-50° shell was discontinued at $\underline{l} = 7$ due to a very low percentage of reflexions with $\underline{I} > 3\sigma(\underline{I})$. A check reflexion was monitored every 40 reflexion throughout the data collection. The intensity of the check reflexion remained within 10% of its

original value during the data collection, the final measurement giving 95% of the original count. Lorentz and polarization corrections and check reflexion scaling were applied in deriving the structure amplitudes. No absorption correction was made in view of the relatively small value of μ. Of the 2352 independent reflexions measured, 1113 had intensities less than $3\sigma(\underline{I})$ above background where $\sigma^2(\underline{I}) = \underline{S} + \underline{B} + (0.03\underline{S})^2$ with $\underline{S}$ = scan count and $\underline{B}$ = time averaged background count. These reflexions were not included in the refinement.

Structure Analysis

The positions of the two molybdenum atoms were determined from the three-dimensional Patterson function. One cycle of isotropic full-matrix least-squares refinement gave $\underline{R}$ 0.25. A subsequent difference map revealed three large peaks, two of which were clearly the bridging aluminum atoms. The third peak was thought to be anomalous at the time and was left out of the calculations. The molybdenum and two aluminum atoms were refined isotropically for one cycle and a second difference Fourier was calculated. The $\underline{R}$ factor at this point was 0.200. The difference map showed the same large peak as the previous one, which was deduced to be a third aluminum atom, as well as probable positions for sixteen carbon atoms. The molybdenum atoms were then refined anisotropically and the three aluminum and sixteen carbon atoms isotropically for one cycle, giving $\underline{R}$ 0.130. After one additional cycle of refinement and difference Fourier

synthesis all 25 carbon atoms had been located. Refinement with anisotropic carbon atoms gave an R value of 0.051 but three carbon atoms had non-positive definite temperature factors. Since the number of strong reflexions was relatively low it was decided to refine the structure with isotropic thermal parameters for the carbon atoms.

Hydrogen atom positions were calculated with C-H = 0.97 Å for the methyl and cyclopentadienyl groups. The hydrogen atoms were assigned isotropic temperature factors approximately 1.5 Å² larger than the mean B for the carbon atom type to which they are bonded. Difference maps did not unambiguously reveal the position of the molybdenum hydrogen atoms. With the 33 methyl and cyclopentadienyl hydrogen atoms fixed, the remainder of the structure was refined to convergence with the carbon atoms isotropic, Mo and Al atoms anisotropic. The final agreement factors were R 0.066 and Rw 0.063 for 1213 reflexions with $I > 3\sigma(I)$.

The absolute configuration of the complex (for the particular crystal used) has been determined through the anomalous scattering of the molybdenum and aluminum atoms. Enantiomorph (A) is represented by the coordinates in Tables 40 and 42. Enantiomorph (B) was generated by changing the x coordinates of (A) to 1-x. (B) was then refined to convergence and Hamilton's test (24) was applied to the resulting R factor ratios. The results, summarized in Table 43, indicate that enantiomorph (A) is most probably the correct absolute configuration, assuming the data to be free

of systematic error.

The scattering factors of ref. 12 were used for the non-
hydrogen atoms and those of ref. 13 for the hydrogen atoms.
Corrections for anomalous scattering have been made for the
molybdenum and aluminum atoms(13). A standard errors
weighting scheme was used (see Part 3) giving constant
average values of $\underline{w}(\underline{F}o - \underline{F}c)^2$ over ranges of $|\underline{F}o|$ in the final
stages of refinement. On the final cycle of refinement the
largest parameter shift was 0.31σ. Final positional
parameters appear in Table 40 and thermal parameters in Table
41. The calculated positions of the hydrogen atoms and their
assigned temperature factors appear in Table 42. In the final
stages of refinement 26 reflexions believed to be suffering
from counter errors or which had ratios of greater than 10:1
between the two background counts were given zero weight.
Observed and calculated structure amplitudes are available on
request.

RESULTS AND DISCUSSION

Bond distances and angles appear in Tables 44 and 45
respectively. Weighted least-squares mean planes are given in
Table 46 and some important non-bonded contacts in Table 47.
Table 48 gives structural data for related molybdenum
cyclopentadienyl complexes. Stereoscopic views of the
structure viewed along the $\underline{c}$ and $\underline{b}$ axes are shown in Figures
14 and 15.

The crystal structure consists of discrete molecular

Table 40

Final positional parameters (fractional x 10^4)

with estimated standard deviations in parentheses

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$
Mo(1)	4031(1)	9007(1)	5698(2)
Mo(2)	2971(1)	6488(1)	3182(2)
Al(1)	3720(2)	8025(4)	3296(7)
Al(2)	3440(3)	7152(4)	6166(6)
Al(3)	5033(3)	7308(4)	2544(8)
C(1)	3610(8)	8777(11)	1476(20)
C(2)	2652(9)	7157(12)	7586(21)
C(3)	4111(9)	6284(11)	7097(19)
C(4)	5311(12)	7847(17)	585(30)
C(5)	5728(10)	6463(15)	3457(24)
C(11)	4825(8)	8301(12)	4091(20)
C(12)	4980(10)	8119(14)	5585(26)
C(13)	5159(10)	8891(15)	6371(22)
C(14)	5093(11)	9578(15)	5439(27)
C(15)	4895(9)	9309(12)	4061(22)
C(21)	4121(8)	6588(12)	2430(18)
C(22)	3675(9)	6443(14)	1167(20)
C(23)	3358(11)	5571(15)	1344(24)
C(24)	3548(10)	5133(13)	2729(24)
C(25)	4013(9)	5804(11)	3290(20)
C(31)	2859(10)	9264(12)	6137(20)
C(32)	3082(12)	9808(15)	4941(25)
C(33)	3592(12)	10424(17)	5446(30)
C(34)	3646(12)	10331(17)	6871(31)
C(35)	3220(11)	9617(15)	7415(25)
C(41)	1845(11)	6082(16)	3250(30)
C(42)	1906(10)	6793(14)	4219(25)
C(43)	2123(12)	7557(15)	3564(26)
C(44)	2152(10)	7337(13)	2022(25)
C(45)	1967(11)	6402(15)	1954(26)

Table 41

Final thermal parameters and

their estimated standard deviations

(a) Anisotropic thermal parameters ($\underline{U}_{11}$ x 100 Å^2)

Atom	$\underline{U}_{11}$	$\underline{U}_{22}$	$\underline{U}_{33}$	$\underline{U}_{12}$	$\underline{U}_{13}$	$\underline{U}_{23}$
Mo(1)	2.7(1)	2.8(1)	3.5(1)	0.3(1)	0.3(1)	-0.5(1)
Mo(2)	2.4(1)	3.2(1)	3.9(1)	-0.4(1)	-0.1(1)	-0.2(1)
Al(1)	3.1(3)	2.6(3)	3.4(4)	-0.1(2)	0.0(3)	0.3(3)
Al(2)	3.9(4)	5.0(4)	2.4(4)	0.7(3)	0.3(3)	1.1(3)
Al(3)	3.2(3)	5.6(4)	6.5(4)	-0.4(3)	1.6(3)	-2.0(4)

(b) Isotropic thermal parameters

Atom	$\underline{B}$ (Å^2)	Atom	$\underline{B}$ (Å^2)
C(1)	3.3(4)	C(23)	5.0(5)
C(2)	3.3(4)	C(24)	4.2(5)
C(3)	3.4(4)	C(25)	3.1(4)
C(4)	7.1(6)	C(31)	3.4(4)
C(5)	5.5(5)	C(32)	5.4(6)
C(11)	2.6(4)	C(33)	6.5(6)
C(12)	4.5(5)	C(34)	6.8(6)
C(13)	4.4(5)	C(35)	5.0(5)
C(14)	4.9(5)	C(41)	5.8(6)
C(15)	3.4(4)	C(42)	4.6(5)
C(21)	2.7(4)	C(43)	5.8(6)
C(22)	3.9(4)	C(44)	4.5(5)
		C(45)	5.1(5)

Table 42

(a) Calculated hydrogen atom positions* (fractional x 10⁴)

   and assigned isotropic temperature factors

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$	$\underline{B}$ $(\overset{\circ}{A}{}^2)$
H(1A)	3164	9078	1488	5.0
H(1B)	3971	9244	1440	5.0
H(1C)	3646	8379	616	5.0
H(2A)	2290	7572	7195	5.0
H(2B)	2475	6554	7715	5.0
H(2C)	2808	7417	8529	5.0
H(3A)	4507	6213	6454	5.0
H(3B)	4256	6531	8044	5.0
H(3C)	3892	5687	7242	5.0
H(4A)	5718	8229	720	7.5
H(4B)	5413	7349	-98	7.5
H(4C)	4938	8221	201	7.5
H(5A)	6135	6817	3719	7.5
H(5B)	5533	6179	4328	7.5
H(5C)	5852	5987	2743	7.5
H(12)	4965	7499	6012	5.5
H(13)	5300	8922	7400	5.5
H(14)	5177	10220	5704	5.5
H(15)	4817	9712	3216	5.5
H(22)	3605	6870	349	5.5
H(23)	3051	5296	617	5.5
H(24)	3399	4547	3149	5.5
H(25)	4243	5719	4232	5.5
H(31)	2527	8758	6110	6.5
H(32)	2917	9764	3930	6.5
H(33)	3856	10854	4843	6.5
H(34)	3945	10705	7501	6.5
H(35)	3175	9405	8432	6.5
H(41)	1723	5446	3483	6.5
H(42)	1808	6742	5264	6.5
H(43)	2233	8144	4034	6.5
H(44)	2277	7747	1212	6.5
H(45)	1935	6046	1038	6.5

continued...

(b) Cyclopentadienyl ring centroid coordinates

(fractional x 10^4)

Ring	$\underline{x}$	$\underline{y}$	$\underline{z}$
R(1)	4990	8840	5109
R(2)	3743	5908	2192
R(3)	3280	9889	6162
R(4)	1999	6834	3002

* The hydrogen atoms are labelled as follows: the cyclopentadienyl hydrogens have the same number as the carbon atom to which it is bonded, e.g. H(12) is bonded to C(12); the methyl hydrogens are denoted by a numeral referring to the carbon atom to which it is bonded and by A, B, or C to distinguish between the three different hydrogens associated with each carbon.

Table 43

Results of Hamilton's Test

Parameter compared	Value for enantiomorph (A)	(B)	(B/A)	Sig. level[1]
Conventional R (3σ data)	6.56	6.58	1.0030	97.5
Conventional R (all F)	14.34	14.39	1.0035	99.5
Weighted R (3σ data)	6.31	6.32	1.0022	95.0
Weighted R (all F)	6.51	6.52	1.0021	99.5

[1] This is the % probability that enantiomorph (A) is the correct absolute configuration.

units with normal van der Waals contacts between units. The
closest intermolecular contacts, including those for hydrogen
atoms in calculated positions, are listed in Table 47.
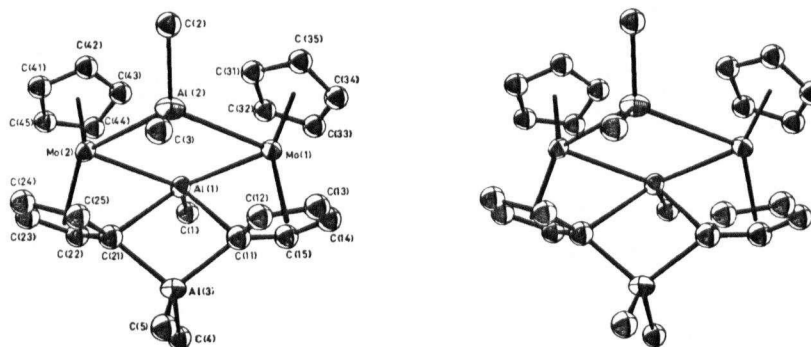
Figure 13

A stereoscopic view of the $C_{25}H_{35}Al_3Mo_2$
molecule. 50% probability ellipsoids are
shown for Mo and Al atoms. Carbon atoms
are represented by equivalent spheres.

The molecular structure exhibits several unusual and
novel features. The three aluminum atoms in the molecule are
of different structural types. One of them, Al(2), was of the
predictable dimethylaluminum type, bridging two molybdenum
atoms. The distances Mo(1)-Al(2) and Mo(2)-Al(2) are 2.944(6)
and 3.003(6) Å. The Mo(1)-Al(2)-Mo(2) angle is 106.2(2)°
while the opposite angle C(2)-Al(2)-C(3) is 103.9(7)°. Thus
the coordination about Al(2) is that of a distorted
tetrahedron. Other angles at Al(2) range from 110.5 to
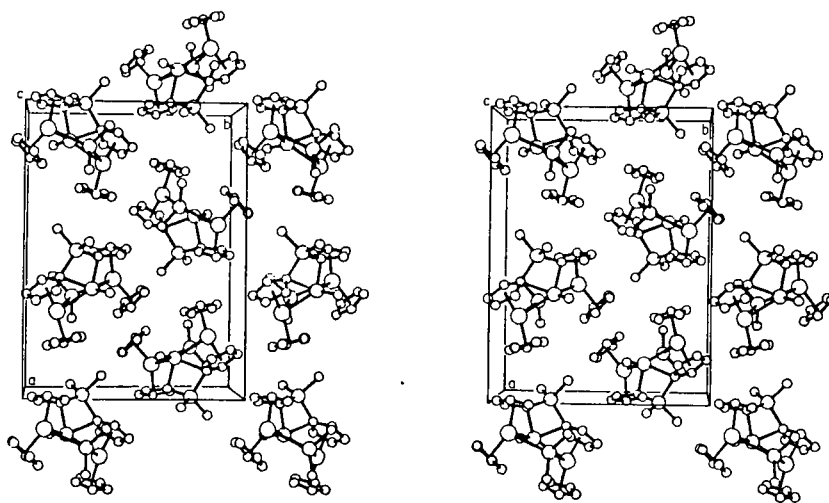
Figure 14

The structure viewed down c.
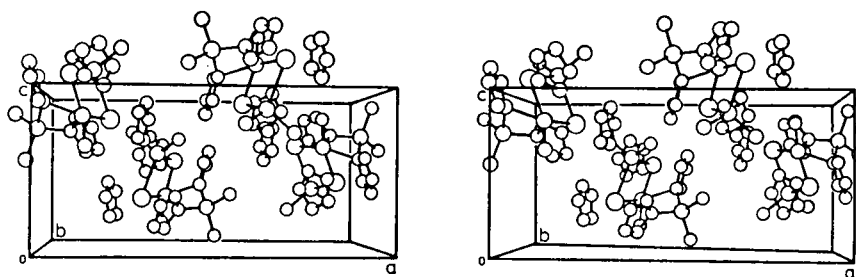

Figure 15

The structure viewed along b.

Table 44

Bond lengths (Å) with estimated

standard deviations in parentheses

Atoms	distance	Atoms	distance
Mo(1)-Al(1)	2.662(6)	Al(1)-C(1)	1.98(2)
Mo(2)-Al(1)	2.655(5)	Al(1)-C(11)	2.30(2)
Mo(1)-Al(2)	2.944(6)	Al(1)-C(21)	2.35(2)
Mo(2)-Al(2)	3.003(6)	Al(2)-C(2)	2.00(2)
Mo(1)-C(11)	2.35(2)	Al(2)-C(3)	1.99(2)
Mo(1)-C(12)	2.25(2)	Al(3)-C(4)	2.01(3)
Mo(1)-C(13)	2.28(2)	Al(3)-C(5)	2.00(2)
Mo(1)-C(14)	2.23(2)	Al(3)-C(11)	2.04(2)
Mo(1)-C(15)	2.28(2)	Al(3)-C(21)	2.05(2)
Mo(1)-C(31)	2.34(2)	C(11)-C(12)	1.41(3)
Mo(1)-C(32)	2.28(2)	C(12)-C(13)	1.37(3)
Mo(1)-C(33)	2.23(2)	C(13)-C(14)	1.31(3)
Mo(1)-C(34)	2.31(2)	C(14)-C(15)	1.36(3)
Mo(1)-C(35)	2.38(2)	C(15)-C(11)	1.46(2)
Mo(2)-C(21)	2.34(2)	C(21)-C(22)	1.45(2)
Mo(2)-C(22)	2.28(2)	C(22)-C(23)	1.41(3)
Mo(2)-C(23)	2.25(2)	C(23)-C(24)	1.45(3)
Mo(2)-C(24)	2.29(2)	C(24)-C(25)	1.42(2)
Mo(2)-C(25)	2.25(2)	C(25)-C(21)	1.39(2)
Mo(2)-C(41)	2.26(2)	C(31)-C(32)	1.40(2)
Mo(2)-C(42)	2.31(2)	C(32)-C(33)	1.41(3)
Mo(2)-C(43)	2.28(2)	C(33)-C(34)	1.30(3)
Mo(2)-C(44)	2.26(2)	C(34)-C(35)	1.41(3)
Mo(2)-C(45)	2.25(2)	C(35)-C(31)	1.44(3)
Mo(1)-R(1)	1.95	C(41)-C(42)	1.35(3)
Mo(2)-R(2)	1.94	C(42)-C(43)	1.32(3)
Mo(1)-R(3)	1.98	C(43)-C(44)	1.43(3)
Mo(2)-R(4)	1.96	C(44)-C(45)	1.40(2)
		C(45)-C(41)	1.28(3)

Table 45

Bond angles (deg) with estimated

standard deviations in parentheses

Atoms	angle	Atoms	angle
Al(1)-Mc(1)-Al(2)	62.9(2)	C(15)-C(11)-C(12)	101(2)
Al(1)-Mo(1)-R(1)	85.9	C(15)-C(11)-Al(1)	105(1)
Al(1)-Mo(1)-R(3)	110.4	C(15)-C(11)-Al(3)	132(1)
Al(2)-Mo(1)-R(1)	107.3	C(12)-C(11)-Al(1)	118(1)
Al(2)-Mo(1)-R(3)	105.5	C(12)-C(11)-Al(3)	119(1)
R(1)-Mo(1)-R(3)	147.1	Al(1)-C(11)-Al(3)	81.3(6)
Al(1)-Mo(2)-Al(2)	62.1(2)	C(25)-C(21)-C(22)	104(2)
Al(1)-Mo(2)-R(2)	87.5	C(25)-C(21)-Al(1)	119(1)
Al(1)-Mo(2)-R(4)	108.5	C(25)-C(21)-Al(3)	121(1)
Al(2)-Mo(2)-R(2)	108.6	C(22)-C(21)-Al(1)	101(1)
Al(2)-Mo(2)-R(4)	106.6	C(22)-C(21)-Al(3)	129(1)
R(2)-Mo(2)-R(4)	144.8	Al(1)-C(21)-Al(3)	79.6(6)
C(1)-Al(1)-Mo(1)	114.2(5)	C(11)-C(12)-C(13)	114(2)
C(1)-Al(1)-Mo(2)	111.5(5)	C(12)-C(13)-C(14)	105(2)
C(1)-Al(1)-C(11)	105.4(7)	C(13)-C(14)-C(15)	114(2)
C(1)-Al(1)-C(21)	104.1(7)	C(14)-C(15)-C(11)	107(2)
Mo(1)-Al(1)-Mo(2)	126.9(2)	C(21)-C(22)-C(23)	107(2)
Mo(1)-Al(1)-C(11)	56.0(4)	C(22)-C(23)-C(24)	112(2)
Mo(1)-Al(1)-C(21)	131.8(5)	C(23)-C(24)-C(25)	100(2)
Mo(2)-Al(1)-C(11)	131.9(5)	C(24)-C(25)-C(21)	117(2)
Mo(2)-Al(1)-C(21)	55.2(4)	C(35)-C(31)-C(32)	106(2)
C(11)-Al(1)-C(21)	87.1(6)	C(31)-C(32)-C(33)	109(2)
Mo(1)-Al(2)-Mo(2)	106.2(2)	C(32)-C(33)-C(34)	108(2)
Mo(1)-Al(2)-C(2)	112.0(6)	C(33)-C(34)-C(35)	112(2)
Mo(1)-Al(2)-C(3)	112.3(5)	C(34)-C(35)-C(31)	105(2)
Mo(2)-Al(2)-C(2)	110.5(6)	C(45)-C(41)-C(42)	108(2)
Mo(2)-Al(2)-C(3)	112.1(6)	C(41)-C(42)-C(43)	112(2)
C(2)-Al(2)-C(3)	103.9(7)	C(42)-C(43)-C(44)	105(2)
C(4)-Al(3)-C(5)	114.8(10)	C(43)-C(44)-C(45)	104(2)
C(4)-Al(3)-C(11)	112.6(9)	C(44)-C(45)-C(41)	111(2)
C(4)-Al(3)-C(21)	112.6(9)		
C(5)-Al(3)-C(11)	106.2(8)		
C(5)-Al(3)-C(21)	107.1(8)		
C(11)-Al(3)-C(21)	102.7(7)		

112.3°, the mean angle at Al(2) being 109.5°.

The two remaining aluminum atoms are involved in the unique structural feature of this system. Instead of a second bridging $AlMe_2$ unit an AlMe group bridges the two molybdenum atoms and at the same time is involved in a novel multicentre bonding arrangement with the two unique carbon atoms of the C_5H_4 groups, C(11) and C(21), and the remaining aluminum atom, Al(3), which occurs as an $AlMe_2$ unit. The two Al(1)-Mo distances, 2.662(6) and 2.657(5) Å, are equal to within experimental error. The fact that these distances are more than 0.3 Å shorter than the corresponding Al(2)-Mo bonds has interesting structural implications which will be discussed. The Al_2Mo_2 bridging system is significantly non-planar (see Table 46). The angle between the normals to the two AlAlMo planes is 168.9°. The Al(1)-Al(3) and Mo(1)-Mo(2) distances are 2.935(8) and 4.757(2) Å respectively, neither of which represents any direct interaction. The remaining angles in this system are Mo(1)-Al(1)-Mo(2), 129.9(2), Al(1)-Mo(1)-Al(2), 62.9(2), and Al(1)-Mo(2)-Al(2), 62.1(2)°.

Bond angles at Al(1) involving the two molybdenum atoms, C(1), and Al(3) have a mean value of 108.2°. This is indicative that Al(1) is sp³ hybridized with three hybrids nearly parallel to the two Al(1)-Mo and Al(1)-C(1) bonds, and the remaining hybrid, which is involved in the multicentre bonding, directed toward Al(3). The Al(1), C(11), C(21), Al(3) multicentre bonding arrangement resembles that in the trimethylaluminum dimer (68), although closer examination

reveals unique differences. The $[(CH_3)_3Al]_2$ structure is centrosymmetric with a planar bridging arrangement; the two independent Al-C(bridge) distances are 2.125 and 2.123 Å, and Al-C(terminal) are 1.949 and 1.956 Å. The angles in the bridge portion are 75.7° at C and 104.3° at Al. The bridge system in the present structure is non-planar (see Table 46), the angle between the two AlAlC planes is 149.7°, and also asymmetric with short bonds to Al(2), mean Al(2)-C(bridge) = 2.05 Å, and long bonds to Al(1), mean Al(1)-C(bridge) = 2.33 Å. The angles in the bridge are 87.1(6) at Al(1), 102.7(7) at Al(3), 79.7(6) at C(21), and 81.3(6)° at C(11). Figure 16 shows a schematic representation of the atomic orbitals believed to be involved in the multicentre bonding: one sp^2 hybrid orbital from each of C(11) and C(21), one sp^3 hybrid orbital from Al(1) and two sp^3 hybrid orbitals from Al(3). Note that Al(1) lies twice as far from the mean planes of the C_5H_4 rings (represented by the horizontal dotted lines in Figure 16) as does Al(3). The bonding scheme represented by Figure 16 is adequate to explain the observed geometry of the system, particularly the difference between the Al(1)-C(bridge) and Al(3)-C(bridge) distances.

The coordination about Al(3) is a somewhat distorted tetrahedron, with the angle C(4)-Al(3)-C(5) expanded to 114.8(10)° corresponding to the contraction of the opposite angle, C(11)-Al(3)-C(21), to 102.7(7)°. Other angles at Al(3) range from 106.2 to 112.6°, and the mean of all angles at Al(3) is 109.3°. None of the five Al-C(terminal) distances differs significantly from the mean value of 2.00(1) Å, which
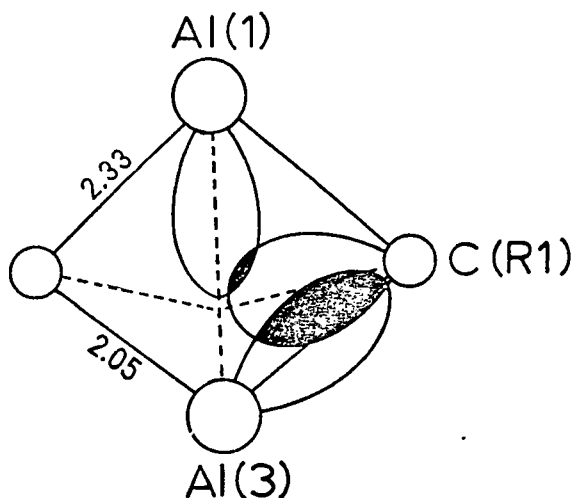
Figure 16

A representation of the bonding in the
Al(1)-C(11)-C(21)-Al(3) bridging system.
Mean bond distances are shown.

is equal to the sum of covalent radii.

The two C_5H_5 and two C_5H_4 groups are all <u>pentahapto</u> to

the molybdenum atoms, and, assuming that one hydrogen atom is

also coordinated to each of the molybdenum atoms, the latter

obey the 18-electron rule. If the C_5H_5 and C_5H_4 groups are

regarded as formally negatively charged and occupying three

coordination sites at the metal atom, the complex may be

regarded as a nine-coordinate complex of Mo(II) (assuming the

H atom is a one electron donor). The recently reported

structure of the niobocene dimer $[(C_5H_5)(C_5H_4)NbH]_2$ (69) also

contains <u>monohapto</u> and <u>pentahapto</u> C_5H_4 ligands. The present

Table 46

Weighted least-squares mean planes

(a) Distances (Å) of relevant atoms from the mean planes

Atom	d	d/σ		Atom	d	d/σ
Plane 1: C(11)-C(15)				**Plane 3: C(31)-C(35)**		
C(11)	0.011	0.7		C(31)	0.012	0.6
C(12)	-0.019	1.0		C(32)	-0.024	1.1
C(13)	0.011	0.6		C(33)	0.028	1.1
C(14)	0.000	0.0		C(34)	-0.013	0.6
C(15)	-0.008	0.4		C(35)	-0.005	0.2
Mo(1)	-1.951	1296.3		Mo(1)	1.976	1304.8
Plane 2: C(21)-C(25)				**Plane 4: C(41)-C(45)**		
C(21)	0.008	0.5		C(41)	-0.024	1.2
C(22)	-0.014	0.8		C(42)	0.024	1.2
C(23)	0.016	0.8		C(43)	-0.023	1.0
C(24)	-0.006	0.3		C(44)	0.007	0.3
C(25)	-0.003	0.2		C(45)	0.008	0.4
Mo(2)	-1.934	1278.7		Mo(2)	-1.956	1339.1
Plane 5: Mo(1&2), Al(1&2)				**Plane 6: Al(1&3), C(11&12)**		
Mo(1)	-0.017	11.5		Al(1)	0.033	5.7
Mo(2)	-0.017	11.3		Al(3)	0.064	9.4
Al(1)	0.240	49.4		C(11)	-0.390	22.2
Al(2)	0.176	30.8		C(21)	-0.375	22.3

(b) Equations of planes: $\ell X + m Y + n Z = p$, where X, Y, and Z are orthogonal angstrom coordinates derived as follows:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Plane	ℓ	m	n	p
1	0.9605	-0.1070	-0.2570	6.7463
2	0.7566	-0.4539	-0.4707	0.6892
3	0.7270	-0.6674	-0.1612	-5.8012
4	-0.9584	0.2596	-0.1189	-1.4746
5	0.8852	-0.4608	-0.0635	0.6188
6	-0.0060	0.5164	-0.8563	-3.3572

(c) Angles between plane normals

Planes	angle	Planes	angle	Planes	angle
(1)-(2)	154	(2)-(3)	158	(3)-(5)	164
(1)-(3)	144	(2)-(4)	142	(3)-(6)	102
(1)-(4)	157	(2)-(5)	155	(4)-(5)	164
(1)-(5)	156	(2)-(6)	81	(4)-(6)	104
(1)-(6)	81	(3)-(4)	148	(5)-(6)	101

Table 47

Selected intra- and intermolecular contacts

Intramolecular		Intermolecular*	
Atoms	**distance**	**Atoms**	**distance**
Mo(1)...Mo(2)	4.757(2)	C(13)...C(14) [1]	3.29(3)
Al(1)...Al(2)	2.935(8)	C(1)...H(35) [2]	3.02
Al(1)...Al(3)	2.831(8)	C(2)...H(22) [3]	3.14
C(11)...C(21)	3.20(2)	C(3)...H(14) [4]	2.87
C(15)...C(33)	3.25(3)	C(23)...H(41) [5]	2.98
C(23)...C(45)	3.00(3)	C(41)...H(23) [6]	2.93
C(33)...C(14)	3.16(3)	H(2B)...H(24) [6]	2.36
C(34)...C(14)	3.28(3)	H(2C)...H(22) [3]	2.39
C(2)...H(31)	2.66	H(3C)...H(41) [6]	2.31
C(2)...H(42)	2.73		
C(3)...H(12)	2.60		
C(3)...H(25)	2.73		
C(31)...H(43)	2.77		
H(1B)...H(15)	2.39		
H(1C)...H(22)	2.19		
H(2A)...H(31)	2.07		
H(2A)...H(42)	2.31		
H(3A)...H(12)	2.10		
H(3A)...H(25)	2.19		
H(31)...H(43	2.15		

*Superscripts refer to atoms at positions:

[1]	1/2+x	3/2-y	1-z	[4]	1-x	y-1/2	3/2-z
[2]	x	y	z-1	[5]	1/2-x	1-y	z-1/2
[3]	x	y	z+1	[6]	1/2-x	1-y	1/2+z

Table 48

Structural data for some

molybdenum cyclopentadienyl complexes

Compound	Mo-C (Cp)	C-C (Cp)	Mo-centroid
a	2.285	1.389	1.96
b	---	1.40-1.44	---
c	2.333	1.413	---
d	2.333	1.412	---
e	2.310	1.378	---
f	2.32-2.68	1.347-1.427	---
g	2.34	1.41	2.08
h	2.30	---	1.97
i	2.35	1.42	2.01
j	2.338	1.418	2.00
k	2.324	1.421	---
l	---	1.39	2.02
m	2.289	1.425	1.94
n	2.345	1.416	---
o	2.38	1.43	2.04
p	2.329	1.391	2.00
q	2.253-2.368	1.385	1.999,1.993
r	2.32-2.39	1.405	---
s	2.229-2.388	1.396	1.976,2.002
t	---	1.41	---
u	2.244-2.396	1.394	1.980,1.981
v	2.21-2.42	1.40	1.96-2.01
w	2.27-2.36	1.27-1.42	1.986,1.993
x	2.26-2.40	1.40	1.962,1.991

a. $C_{25}H_{35}Al_3Mo_2$, this work

b. $(C_5H_4)(C_5H_5)(CO)MoMn(CO)_4$, ref. 72

c. $(C_5H_5)Mo(CO)(PPh_3)_2(NCO)$, ref. 75

d. $(C_5H_5)Mo(CO)_2(PPh_3)I$, ref. 76

e. $(C_5H_5)Mo(CO)(Ph_2PCH_2CH_2PPh_2)Cl$, ref. 76

f. $(C_5H_5)_3Mo(NO)$, ref. 77

g. $Mo(C_5H_5)(CO)_5(CH_2SCH_3)$, ref. 78

h. $[Mo(C_5H_5)(SCH_3)_2]_2$, ref. 79

I. $(C_5H_5)Mo(CO)_3CH_2COOH$, ref. 80

j. $[PPh_4]^+ [(C_5H_5)Mo\{S_2C_2(CN)_2\}_2]^-$, ref. 81

k. $(C_5H_5)Mo(CO)(Ph_2PCH_2)_2Cl$, ref. 82

l. $(C_5H_5)_2MoS_2C_6H_4$, ref. 83

m. $(C_5H_5)_2MoH_2$, ref. 71

n. $[(C_5H_5)Mo(CO)_3]_2$, ref. 84

o. $(C_5H_5)Mo(CO)_3C_2H_5$, ref. 85

p. $[(C_5H_5)Mo(CO)_2]_2(H)[P(CH_3)_2]$, ref. 86

q. $(C_5H_5)_2MoS_2C_6H_3CH_3$, ref. 87

r. $C_5H_5(CO)_2\overline{MoN(H)NC(CO_2C_2H_5)C}OH$, ref. 88

s. $(C_5H_5)_2MoS(CH_2)_2NH_2I$, ref. 89

t. $(C_5H_5(CO)_2MoN.N(CH_3).C(CO_2C_2H_5)COH)PF_6$, ref. 90

u. $H[(C_5H_5)_2\overline{MoNH_2CH(CH_2S})COO]Cl$, ref. 91

v. $H[(C_5H_5)_2\overline{MoNH_2CH(CH_2S})COO]PF_6$, ref. 91

w. $[(C_5H_5)_2\overline{MoNH_2CH_2COO}]Cl.H_2O$, ref. 91

x. $[(C_5H_5)_2\overline{MoHN(CH_3)CH_2COO}]Cl.CH_3OH$, ref. 91

structure again demonstrates the versatility of the C_5H_5 ligand in that the C_5H_4 groups derived therefrom are pentahapto to a molybdenum atom and are involved via the unique carbon atom in multicentre bonding to aluminum atoms.

The mean Mo-C distance is 2.285 Å with individual distances ranging from 2.23 to 2.38 Å and the mean Mo-R (ring centroid) distance is 1.96 Å. The four cyclopentadienyl rings are all planar to within experimental error (see Table 46). The mean C-C bond length in the rings is 1.389 Å and the mean C-C-C angle is, as expected, 108°. The Mo-C, C-C(cyclopentadienyl), and Mo-R distances are in good agreement with those of related compounds which are compiled in Table 48.

The structure may be interpreted in terms of valence bond theory in a manner analogous to that described for the niobocene dimer (69). The latter approach views structures of this type of bis(cyclopentadienyl)-transition metal complex as having canted rings with three hybrid orbitals in the horizontal mirror plane (70) as shown in Figure 17. Some structures which can be rationalized by this scheme are given by Guggenberger (69). Both molybdenum atoms in the present molecule have Al(2) in the Ψ_2 position and Al(1) in the Ψ_1 position, the hydrogen atom is assumed to be in the Ψ_3 position. The angles between the C_5H_5 and C_5H_4 planes are 32.9° at Mo(1) and 35.2° at Mo(2), which are similar to those in other molybdenum complexes, e.g. 34° in Cp_2MoH_2 (71) and 35° in $(Cp)(CO)Mo(C_5H_4)Mn(CO)_4$ (72). The length of the two
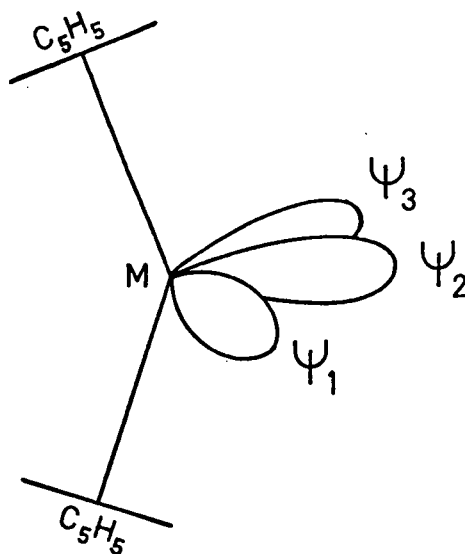
Figure 17

Idealized structure of
bis(cyclopentadienyl)-transition metal
complexes with canted Cp rings.

Mo-Al(2) bonds (0.3 $\overset{\circ}{A}$ longer than the Mo-Al(1) bonds) suggests the possibility of a Mo-H-Al(Me)$_2$-H-Mo bridging system analogous to the Ti-H-AlEt$_2$ system in [(Cp)(C$_5$H$_4$)TiHAlEt$_2$]$_2$ (73,74).

The three aluminum and five methyl carbon atoms are approximately coplanar. The halves of the molecule with respect to this plane are not equivalent, the most interesting difference is that the C$_5$H$_5$ and C$_5$H$_4$ groups associated with Mo(1) are staggered while those at Mo(2) are eclipsed. This results from steric interactions between the Ring 3 and Ring 4 hydrogen atoms. The distance between

calculated positions for H(31) and H(43) is 2.15 $\overset{\circ}{A}$ which is less than the sum of van der Waals radii. If the conformation of the rings were the same at both molybdenum atoms there would be even greater steric interference. Inspection of bond lengths and angles shows other small differences between the two halves of the molecule, some of which are significant. The mean $Mo-C(C_5H_4)$ distances are the same, 2.28 $\overset{\circ}{A}$ for each molybdenum atom, while the Mo-Al(2) distances differ by 10 standard deviations being 3.003(6) $\overset{\circ}{A}$ for Mo(2) and 2.944(6) for Mo(1). The mean Mo-C(Cp) also differ, being 2.31 $\overset{\circ}{A}$ at Mo(1) and 2.27 at Mo(2). The corresponding angles at the two molybdenum atoms show significant differences as well, and may be caused by a small energy difference between the staggered and eclipsed conformations of the C_5H_5 and C_5H_4 rings.

PART 6

THE COMPUTER PROGRAM "SIGCOR"

INTRODUCTION

This section of the thesis describes a computer program which calculates estimated valence bond orders given a set of atomic coordinates. The work is not yet completed but an operational version, which gives satisfactory results when the hybridization at both atoms in the bond involves only s and p orbitals, will be described. Instructions for the use of the program are given and the source deck may be obtained from the author.

The bond order is derived from the fractional difference between the observed interatomic distance and the calculated single bond distance. The calculated value is based on the sum of covalent radii (92) corrected for σ hybridization effects (93-95) and in some cases for electronegativity effects (96). The dependence on electronegativities has not yet been completely worked out.

The program provides qualitatively accurate information about the bonding and electron distribution in the structure. It is intended to serve as an aid in the comparison and analysis of structural information obtained from diffraction and spectroscopic experiments.

GENERAL DESCRIPTION

The program, written in FORTRAN IV, is divided into subroutines to facilitate modification and expansion. The main program performs most of the basic operations, while

subroutine PARSET is a library of covalent radii and electronegativities for a number of commonly occurring atoms. A list is included in the set of instructions. Subroutine ENCOR applies corrections to the covalent radius for electronegativity differences and for formal charges where appropriate. Subroutine BOND is the function which relates bond order to the relative contraction of the bond distance from its calculated value. Finally, subroutine ANGLE is optionally called to calculate and print both the observed valence angles and the calculated angles between the appropriate hybrid orbitals.

The sequence of operations begins with reading the input information. The general atomic coordinates are transformed to orthogonal angstrom coordinates. The covalent radii and electronegativities are assigned by subroutine PARSET for atoms in the library or are read from cards with the atomic positions for atoms not in the library. The internal values may be altered for any particular atom (see instructions). These values are stored in the arrays RAD(i) and CA(i). Bonding information is read in and stored in the form of a symmetric connectivity matrix (97) KB(i,j) where KB(i,j) = 1 if the atoms i and j are bonded to one another and KB(i,j) = 0 otherwise. The hybridization states of "terminal" atoms (those which are univalent) cannot be calculated and are assumed to be $\underline{sp}^3$. If the hybridization state of a terminal atom is known to be different from $\underline{sp}^3$, as in the case of carbonyl groups, this information is read from an optional terminal atom card.

The bond distances and direction cosines of the bonds are then calculated and stored in arrays DB, DL, DM, and DN. The next step is the determination of the fractional s characters, $SF(i,j)$, for the hybrid orbital at atom i involved in the bond between atoms i and j. In general, an orthogonal set of non-equivalent hybrid orbitals which follow the bond directions cannot be constructed from s and p atomic orbitals only. Since the orthogonality conditions must be met, there are usually differences between the interhybrid angles and the observed valence angles if the hybrids are constructed only from s and p atomic orbitals.

The general orthogonality conditions may be expressed as:

$$a_1 a_j + b_1 b_j \cos \theta_{1j} = 1$$

where θ_{1j} is the angle between the non-equivalent hybrids $a_1 \underline{s} + b_1 \underline{p}$ and $a_j \underline{s} + b_j \underline{p}$. It is assumed each of the functions is normalized. This requires:

$$a^2 + b^2 = 1$$

in which case the fractional s and p characters are simply a^2 and b^2.

For divalent atoms it is assumed that the two bonding hybrids are equivalent. In this case the orthogonality condition becomes:

$$a^2 + b^2(\cos \theta) = 0$$

where θ is the bond angle. Since the function is normalized the fractional $\underline{s}$ character (a^2) is given by:

$$SF = \cos \theta/(\cos \theta - 1)$$

trigonometric identities transform this expression to the equivalent form:

$$SF = 1 - 0.5[\csc^2(\theta/2)]$$

which is used in the program. The resulting hybrid orbitals follow the bond directions.

For trigonally coordinated atoms the values of $SF(i,j)$ are calculated using the same formula as for divalent atoms. In this case θ is taken as the mean valence angle at atom i involving the bond i-j. This approach yields non-equivalent hybrid orbitals which satisfy the orthogonality conditions, implying that the total $\underline{s}$ character at a given centre must equal 1. This includes vacant, lone-pair, or π bonding orbitals for which the $\underline{s}$ character is not explicitly calculated but may be deduced. The calculated interhybrid angles are not generally the same as the observed angles, but deviations from ideal geometry are always in the same direction.

The approach which gives the best agreement between

calculated interhybrid angles and bond angles for four-
coordinate atoms is based on an initial assumption of
threefold symmetry. The hybrid for which the s character is
being calculated is assumed to be the unique hybrid and the
remaining three are treated as if they were equivalent. Let θ
be the mean bond angle at atom i not involving atom j. The s
character in each of the artificially equivalent hybrid
orbitals is given by the equation derived above. If we denote
this quantity by x, orthogonality requires that:

$$SF(i,j) = 1 - 3x$$

and substitution of the value of x in the above expression
gives:

$$SF(i,j) = 1.5[csc^2(\theta/2)] - 2$$

Except in cases of extreme steric distortion,
application of the above equation to each of the bonds at a
four-coordinate atom yields a set of orthogonal hybrid
orbitals. When the sum of the s characters in the four
hybrids differs by more than 2% from unity, a message to that
effect is printed by the program. The most probable causes
for such deviations are severe steric distortions and
possible involvement of d (or f) orbitals in the makeup of
the bonding hybrids, the latter being most likely for atoms
beyond the first row of the periodic table. As for trivalent
atoms, the hybrids generally do not follow the bond
directions.

The dependence of the single bond distance on the amount of $\underline{s}$ character in the hybrid orbitals involved is a geometric factor, independent of the types of atoms involved. Since the greatest amount of experimental information is available for C-C bonds, they will be used as a standard.

A plot of the percent contraction of the single bond distance (relative to an $\underline{sp}^3$-$\underline{sp}^3$ bond) versus the fractional $\underline{s}$ character of the bonding hybrids is shown in Figure 18. The data points correspond to single C-C bond distances of 1.537, 1.486, and 1.379 Å for $\underline{sp}^3$-$\underline{sp}^3$, $\underline{sp}^2$-$\underline{sp}^2$, and $\underline{sp}$-$\underline{sp}$ bonds; giving the following relationship between the fractional $\underline{s}$ character, SF(i,j), and the fractional contraction of the covalent radius of atom i in the bond i-j, DELTA(i,j):

$$DELTA(i,j) = 0.4112(SF(i,j) - 0.2500)$$

The corrected single bond distance for the bond i-j is given by:

$$SIGCOR(i,j) = (1 - DELTA(i,j))RAD(i) + (1 - DELTA(j,i))RAD(j)$$

where RAD(i) and RAD(j) have been corrected for formal charges (such as quaternary N and B atoms) and electronegativity differences.

The general relationship between bond contraction and bond order has again been based on the behavior of C-C bonds. The values of 1.537, 1.394, 1.335, and 1.206 Å were used for
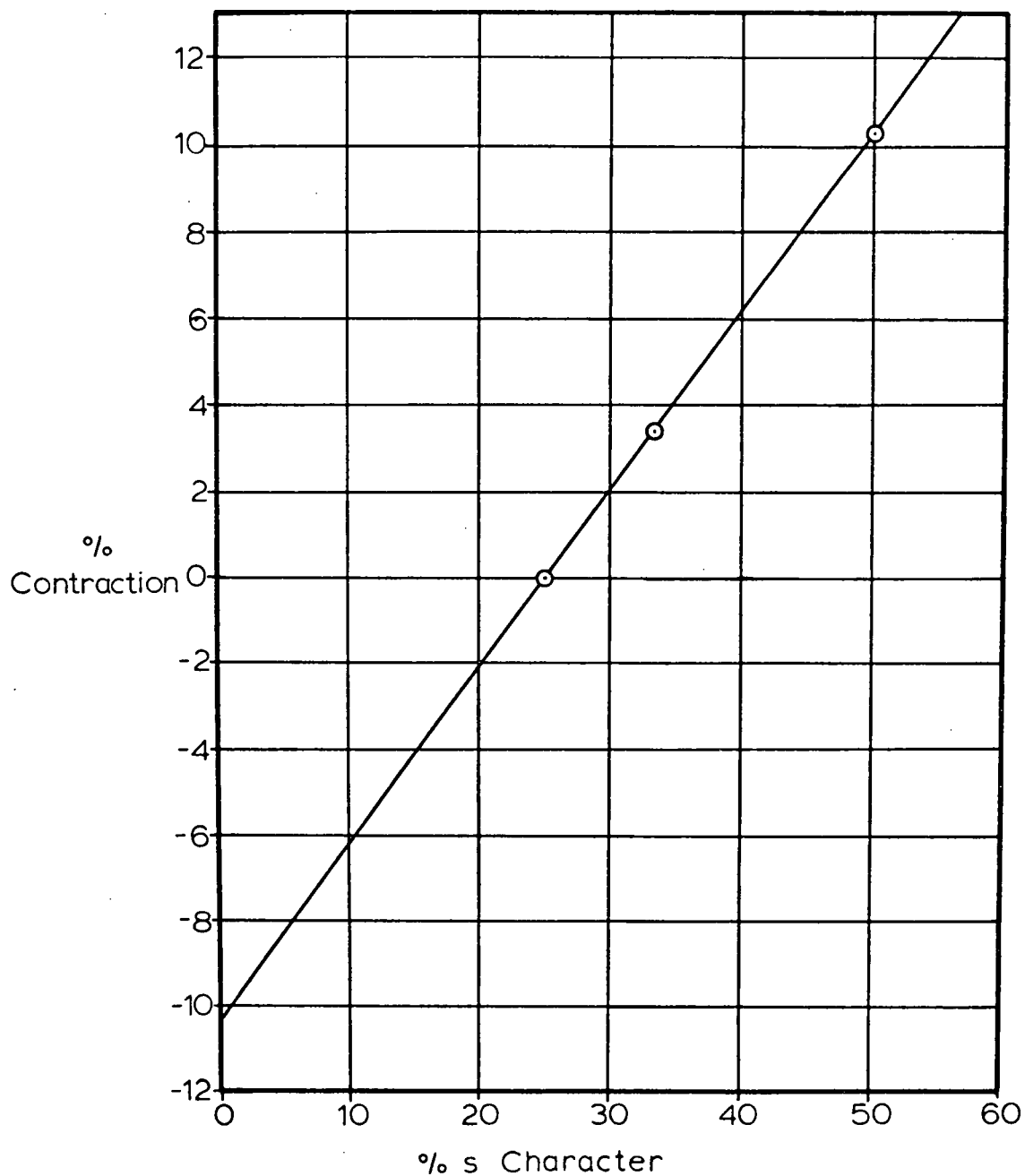
Figure 18

A plot of % contraction of C-C single
bond distances (relative to an sp^3-sp^3
single bond) vs. % s character in the
bonding orbitals.
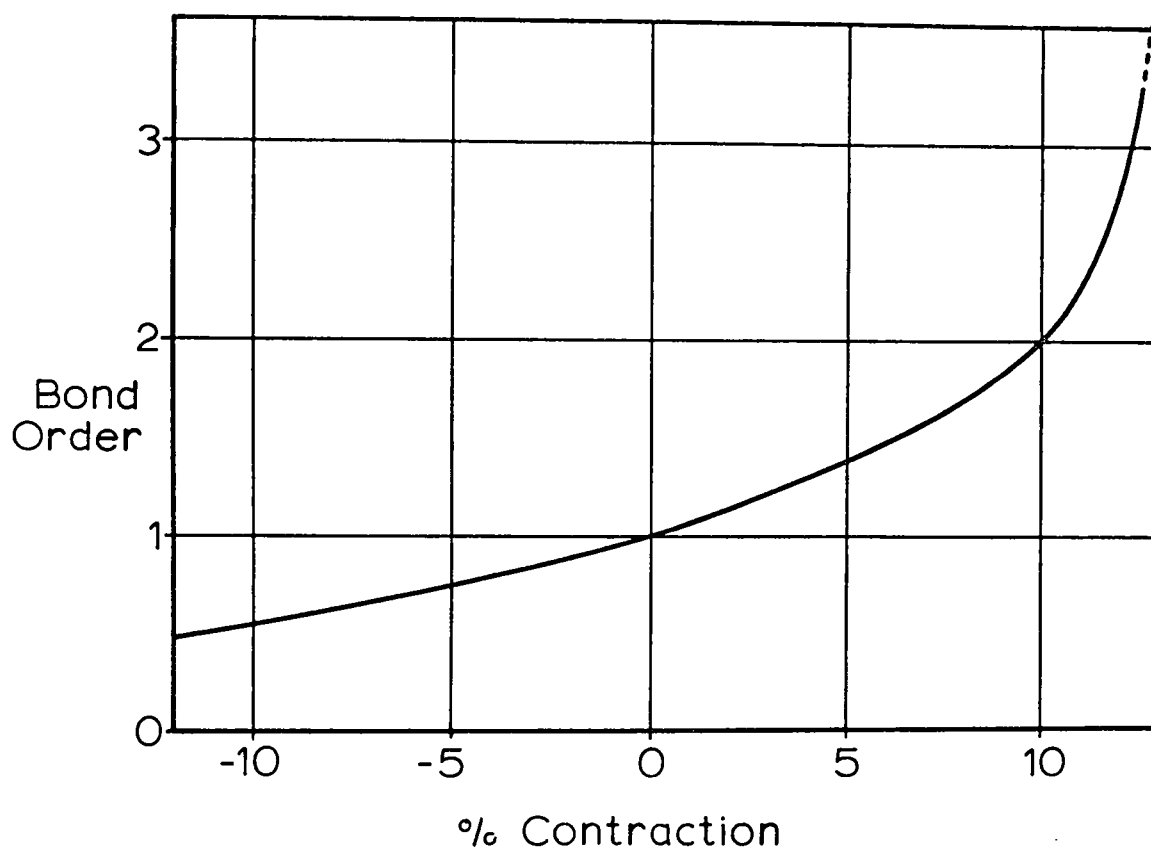
Figure 19

A plot of valence bond order vs. % contraction of the internuclear distance relative to the corrected single bond distance.

formal bond orders of 1, 1.5(aromatic), 2, and 3 respectively. These values were fitted to the following function:

$$x = 2\exp(0.613\ TC - 0.693) \qquad \{TC < 0.47\}$$

$$x = 1 + 1.891\ TC^2 - 1.790\ TC^4 + 0.887\ TC^6 \qquad \{TC \geq 0.47\}$$

where x is the bond order and TC is 10 times the fractional contraction of the bond length. Figure 19 shows a plot of

bond order vs. percent contraction calculated from the above equation. The contraction is relative to the calculated single bond distance.

The printed output begins with a listing of the control parameters followed by the transformation matrix and its inverse. The original input coordinates and the transformed coordinates are listed next. For each chemical bond the following information is given: the observed interatomic distance, the fractional s characters for both of the hybrids involved, the calculated single bond distance, the absolute (A) and percent contractions of the bond relative to the calculated value, the covalent radius used for each of the atoms, the calculated bond order, and finally the derivative of the bond order with respect to a 0.01 Å change in bond length.

In summary, the total calculated bond order for the molecule (excluding bonds involving H) and the number of bonds included in the sum are given. For each non-hydrogen atom the coordination number, sum of calculated s characters, and sum of bond orders are printed. The observed valence angles and calculated interhybrid angles are then (optionally) listed. A sample of the printed output follows the symbolic program listing.

SIGCOR

CALCULATION OF SIGMA HYBRIDIZATION EFFECTS AND

APPROXIMATE BOND ORDERS FROM MOLECULAR GEOMETRY

INPUT

Card 1: Title (20A4)

    1-80   general title card

Card 2: Control Card (6I5)

1-5	NA	number of atoms to be read in (max. 100)
6-10	ND	number of cards in bonding array
11-15	NOUT	= 0 for normal output, 3 to include angles
16-20	NC	= 0 for one card/atom, 1 for two cards
21-25	NTAC	number of terminal atom cards

Card 3: Cell Dimensions in BUCILS format (6F10.5)

1-10	a
11-20	b
21-30	c (Å)
31-40	alpha
41-50	beta
51-60	gamma (degrees)

Card 4: Atomic positions, covalent radii, and

electronegativities (5A2,20X,5F10.6)

If   NC = 0   1 card per atom

         NC = 1   2 cards per atom

Covalent radii and electronegativities (EN) are stored internally for the following atoms:

atom	r	EN	atom	r	EN
B	f(EN)	2.01	Br	1.14	2.74
C	0.768	2.50	I	1.33	2.21
H	0.23	2.20	Si	1.17	1.74
O	0.652	3.50	Sn	1.40	1.72
N	0.701	3.07	Ge	1.22	2.02
P	1.069	2.06	Sb	1.41	1.82
As	1.21	2.20	S	1.04	2.44
F	0.64	4.10	Se	1.17	2.48
Cl	0.99	2.83	Te	1.37	2.01

These are set by the program if the atomic symbol is right justified in columns 3 and 4 of the coordinate card. For atoms in the above list the values punched in the covalent radius and electronegativity fields of the coordinate card are added to the library values. The above values may therefore be changed by punching the desired increment in the appropriate fields (see below). Covalent radius and electronegativity values must be given if the chemical symbol is not in columns 3 and 4 or if the atom is not included in the above list.

The first card for each atom must contain:

    1-10   atom i.d., chemical symbol in cols. 3 and 4

    31-40   x

    41-50   y

    51-60   z (fractional coordinates)

    61-70   covalent radius or change in covalent radius

    71-80   electronegativity

The second card may contain any form of information (e.g. temperature factors) and are ignored by the program.

Card 5: Bonding array (16I3)

ND cards of the form:

    1-3   I   number of reference atom in atoms list

    4-6   JB(n), n = 1, 15

    7-9   numbers in atoms list of atoms bonded to

    10-12   reference atom, if this number is less

    13-15   than I then it should be left out. Each

    16-18   bond is included once.

    etc.

This corresponds to a matrix $B(i,j)$. If the element $B(i,j)$ is non-zero, then the atoms i and j are bonded to each other. Card i in the bonding array input gives the values of j which correspond to non-zero elements in row i of the matrix.

Card 6: Terminal atom corrections (F10.6,20I3)

(Omit if NTAC = 0)

The program assumes sp^3 hybridization for all terminal atoms. If this is not the case these cards are used to set the fractional s character of the atoms in question. SCT is added to 0.2500 to give the desired fractional s character.

    1-10   SCT

   11-13   numbers in atoms list of terminal

   14-16   atoms with hybridization corresponding

   17-19   to the value of SCT in col. 1-10

   etc.   (up to 20 atoms)

For example, if SCT = 0.08333 then the atoms corresponding to the numbers punched in columns 11-13 etc. will have sp^2 hybridization states.

Execution time on the IBM/370 are on the order of 0.5 s for a typical structure (30 atoms). Total formal bond orders will tend to be too high if a libration correction has not been made. In most cases this error will not exceed 5%. At present coordination numbers higher than four cannot be dealt with properly although atoms with higher coordination numbers can be input.

SOURCE LISTING

```
C     SIGCOR: A PROGRAM FOR CALCULATING ESTIMATED BOND LENGTHS AND BOND
C     ORDERS CORRECTED FOR SIGMA HYBRIDIZATION EFFECTS
C     WRITTEN IN FORTRAN IV AT THE UNIVERSITY OF BRITISH COLUMBIA, 1972
C     REVISED JULY, 1973
      COMMON NA
      DATA FC,FH,FO,FN,FP,FAS,FF,FCL,FBR,FI,FSI,FGE,FSN,FSB,FS,FSE,FTE/2
     1H C,2H H,2H O,2H N,2H P,2HAS,2H F,2HCL,2HBR,2H I,2HSI,2HGE,2HSN,2H
     1SB,2H S,2HSE,2HTE/
      DATA FB/2H B/
      DIMENSION X(100),Y(100),Z(100),TITLE(20),SIGS(100)
      DIMENSION CA(100),RAD(100),A(5,100)
      DIMENSION KB(100,100),DL(100,100),DM(100,100),DN(100,100)
      DIMENSION SF(100,100),SIGCOR(100,100),DELTA(100,100)
      DIMENSION TOR(100),DB(100,100),NTOT(100),NAT(20),SPT(100),PICOR(10
     ?0,100),PHI(100,100)
   90 FORMAT(' THIS PROGRAM CALCULATES ESTIMATED SIGMA HYBRIDISATION EFF
     1ECTS AND PI CONTRACTIONS, BASED ON THE FOLLOWING ASSUMPTIONS:'/)
   91 FORMAT(10X,' 1: HYBRIDISATION AT BOTH ATOMS INVOLVES ONLY S AND P
     1ORBITALS')
   92 FORMAT(10X,' 2: THE SINGLE BOND COVALENT RADII ARE THOSE GIVEN IN
     1THE ATOMS LIST BELOW')
   93 FORMAT('1')
   94 FORMAT(10X,                                           ' 3: THE AT
     1OMIC POSITIONS ARE CORRECT, I.E. CONTAIN NO SYSTEMATIC ERRORS.',/,
     110X,' 4: THE HYDROGEN RADIUS HAS BEEN CONTRACTED TO BE CONSISTENT
     1WITH XRAY DATA.',/,10X,' 5: RADII OF B AND N ATOMS ARE AUTOMATICAL
     1LY ADJUSTED WHEN THESE ATOMS ARE FORMALLY CHARGED.',/,10X,' 6: THE
     1 RADIUS OF BORON DEPENDS ON THE ELECTRONEGATIVITY OF ITS SUBSTITUE
     1NTS.',/,10X,' 7: BOND ORDER CALCULATIONS ARE ONLY APPROXIMATE AND
     1 FOR BOND ORDERS >2 SMALL ERRORS IN THE BOND DISTANCE',/,13X,' WIL
     1L CAUSE LARGE ERRORS IN THE BOND ORDER.')
   99 FORMAT(20A4)
  100 FORMAT(6F10.5)
  101 FORMAT(//,'ORTHOGONALIZATION MATRIX IS:',31X,'INVERSE MATRIX IS:',
     1/)
  102 FORMAT(3F15.6,15X,3F15.6,/)
  103 FORMAT(//)
  104 FORMAT(6I5)
  105 FORMAT(5A2,20X,5F10.6)
  106 FORMAT(/,'ORTHOGONALISED COORDINATES:',34X,'FRACTIONAL COORDINATES
     1:',//,' NO.  ATOM ID          X             Y            Z',23X
     1,'X',10X,'Y',10X,'Z')
  107 FORMAT(I5,5A2,3(5X,F10.6),10X,3(3X,F8.4))
  108 FORMAT(16I3)
  118 FORMAT('1','ATOM(I)    ATOM(J)        LENGTH    FS(I,J)     FS(J,I)
     1LCORR    PICON     RAD(I)    RAD(J)    ICON    ORDER DORD/DB'//)
  119 FORMAT(10A2,5F10.4,2F10.3,F8.1,2F8.2)
  120 FORMAT(F10.6,20I3)
  124 FORMAT(/' END OF CALCULATION')
  125 FORMAT('1','  ATOM      SUM FS  NO OF BONDS,TOTAL BOND ORDER AT AT
     1OM       COMMENTS')
  126 FORMAT(5A2,F10.4,5X,I3,F10.3)
  130 FORMAT(5A2,F10.4,5X,I3,F10.3,7X,'ASSUMPTION 1 MAY NOT HOLD AT THIS
     1 ATOM')
  131 FORMAT(30X,A30)
  133 FORMAT('NA=',I3,5X,'ND=',I3,5X,'NOUT=',I3,5X,'NC=',I3,5X,'NTAC=',I
     13,5X,'NOPT=',I3)
  134 FORMAT(/,' TOTAL BOND ORDER FOR THE ',I3,' BONDS NOT INVOLVING H I
     1N THE ASSYMMETRIC UNIT IS: ',F5.2,/,'THE TOTAL NUMBER OF BONDS IS:
     1 ',I3)
  999 FORMAT(' EXECUTION TERMINATED ON ERROR')
      PI=3.1415927
      PA=0.4111906
```

```
        TORD=0.00
        NBT=0
        NENH=0
        WRITE(6,90)
        WRITE(6,91)
        WRITE(6,92)
        WRITE(6,94)
        WRITE(6,93)
C       READ IN AND PRINT OUT TITLE CARD
        READ(5,99)  (TITLE(M),M=1,20)
        WRITE(6,99)  (TITLE(M),M=1,20)
C       READ IN CONTROL CARD
        READ(5,104)  NA,ND,NOUT,NC,NTAC,NOPT
        WRITE(6,103)

        WRITE(6,133)  NA,ND,NOUT,NC,NTAC,NOPT
C       READ IN CELL DIMENSIONS AND SET UP BETA AND INVERSE MATRICES
        DOUBLE PRECISION C(12),D,V
        READ(5,100)  (C(J),J=1,6)
        DO 2 J=7,9
        D=PI*C(J-3)/180
        C(J)=DCOS(D)
2       C(J+3)  =DSIN(D)
        V=DSQRT(1.0+2.0*C(7)*C(8)*C(9)-C(7)**2-C(8)**2-C(9)**2)
        V=C(1)*C(2)*C(3)*V
        BA1=C(1)
        BA2=C(2)*C(9)
        BA3=C(3)*C(8)
        BA4=0.0
        BA5=C(2)*C(12)
        BA6=C(3)*(C(7)-C(8)*C(9))/C(12)
        BA7=0.0
        BA8=0.0
        BA9=V/(C(1)*C(2)*C(12))
        DA1=1.0/C(1)
        DA2=-C(9)/(C(1)*C(12))
        DA3=(BA2*BA6-BA3*BA5)/V
        DA4=0.0
        DA5=1.0/(C(2)*C(12))
        DA6=-BA6/(BA5*BA9)
        DA7=0.0
        DA8=0.0
        DA9=1.0/BA9
        WRITE(6,101)
        WRITE(6,102)  BA1,BA2,BA3,DA1,DA2,DA3
        WRITE(6,102)  BA4,BA5,BA6,DA4,DA5,DA6
        WRITE(6,102)  BA7,BA8,BA9,DA7,DA8,DA9
        NB=NA
        IF(NOPT.EQ.1) GO TO 1
        WRITE(6,103)
C       CLEAR ARRAYS
1       DO 8 I=1,NB
        DO 8 J=1,NB
        SF(J,I)=0.0
8       KB(J,I) = 0
        DO 9 I=1,NA
        TOR(I)=0.00
9       RAD(I)=0.00
C       READ IN POSITIONS AND COVALENT RADII, IF NEEDED
C       PRINT ORTHOGONAL COORDINATES AND SINGLE BOND COVALENT RADII
        WRITE(6,106)
        DO 14 I=1,NA
        READ(5,105)  (A(J,I),J=1,5),XP,YP,ZP,RAD(I),CA(I)
        IF(NC.EQ.0) GO TO 13
        READ(5,131)  SIGS(I)
13      X(I)=BA1*XP+BA2*YP+BA3*ZP
        Y(I)=BA5*YP+BA6*ZP
        Z(I)=BA9*ZP
C       ASSIGN COVALENT RADII AND ELECTRONEGATIVITIES
        CALL PARSET(A(2,I),R,CX)
```

```
      CA(I)=CA(I)+CX
      RAD(I)=RAD(I)+R
      WRITE(6,107) I,(A(J,I),J=1,5),X(I),Y(I),Z(I),XF,YF,ZF
   14 CONTINUE
      WRITE (6,103)
C     READ IN BONDING INFORMATION AND SET UP CONNECTIVITY ARRAY (KB)
  606 FORMAT('ATOM NUMBER ',I5,' ON CARD 5( ',I5,' ) EXCEEDS BONDING ARR
     XAY DIMENSIONS, I.E. IS GREATER THAN NB')
      DIMENSION JB(15)
      L=0
   17 READ(5,108) I,(JB(N),N=1,15)
      L=L+1
      IF(I.GT.NA) GO TO 605
      DO 18 N=1,15
      IF(JB(N).GT.NA) GO TO 607
      IF(JB(N).EQ.0) GO TO 21
      KB(JB(N),I)=KB(JB(N),I)+1
      KB(I,JB(N))=KB(JB(N),I)
   18 CONTINUE
   21 IF(L.EQ.ND) GO TO 32
      GO TO 17
  605 WRITE(6,103)
      WRITE(6,606) I,L
      GO TO 998
  607 WRITE(6,103)
      WRITE(6,606) JB(N),L
      GO TO 998
   32 IF(NTAC.EQ.0) GO TO 26
C     READ TERMINAL ATOM HYBRIDIZATION STATES IF DIFFERENT FROM SP3
      DO 12 K=1,NTAC
      READ(5,120) SCT,(NAT(L),L=1,20)
      DO 25 L=1,20
      IF(NAT(L).EQ.0) GO TO 12
      DO 31 J=1,NB
   31 SP(J,NAT(L))=SCT
   25 CONTINUE
   12 CONTINUE
C     NTOT(M) IS NUMBER OF BONDS FORMED BY ATOM (M)
   26 DO 215 I=1,NA
      NNB=0
      DO 214 J=1,NA
  214 NNB=NNB+KB(J,I)
      NTOT(I)=NNB
  215 CONTINUE
C     CALCULATION OF AND STORAGE OF BOND LENGTHS IN ARRAY (DB)
      M=1
      DO 28 I=1,NB
      M=M+1
      IF(M.GT.NB) GO TO 39
      DO 29 J=M,NB
      N=KB(J,I)
      IF(N.EQ.0) GO TO 29
      DELX=X(J)-X(I)
      DELY=Y(J)-Y(I)
      DELZ=Z(J)-Z(I)
      DB(J,I)=SQRT(DELX**2+DELY**2+DELZ**2)
      DB(I,J)=DB(J,I)
      DL(J,I)=DELX/DB(J,I)
      DL(I,J)=-DL(J,I)
      DM(J,I)=DELY/DB(J,I)
      DM(I,J)=-DM(J,I)
      DN(J,I)=DELZ/DB(J,I)
      DN(I,J)=-DN(J,I)
   29 CONTINUE
   28 CONTINUE
C     CALCULATION OF BOND ANGLES AND S CHARACTER ARRAY ELEMENTS
   39 NG=NB-1
      DO 42 J=1,NB
      DO 41 I=1,NB
```

```
            IF(KB(J,I).EQ.0) GO TO 41
            M=I+1
            PHI(I,J)=0.00
            NN=0
            DO 40 K=1,NB
            IF(KB(K,J).EQ.0) GO TO 40
            IF(K.EQ.I) GO TO 40
            NN=NN+1
            COSANG=(DL(J,I)*DL(J,K))+(DM(J,I)*DM(J,K))+(DN(J,I)*DN(J,K))
            BNGLE=ARCOS(COSANG)*180/PI
         44 PHI(I,J)=PHI(I,J)+BNGLE
         40 CONTINUE
            IF(NN.NE.3) GO TO 66
            PHI(I,J)=656.8-PHI(I,J)
            PHI(I,J)=PI*PHI(I,J)/(360*NN)
            GO TO 67
         66 IF(NN.EQ.0) GO TO 64
            PHI(I,J)=PI*PHI(I,J)/(360*NN)
            GO TO 65
         64 SF(I,J)=SF(I,J)+0.2500
            GO TO 410
         65 SF(I,J)=1.0000-(0.5/(SIN(PHI(I,J))**2))
            GO TO 410
         67 SF(I,J)=(1.5/(SIN(PHI(I,J))**2))-2.000
        410 DELTA(I,J)=PA*(SF(I,J)-0.25000)
         41 CONTINUE
         42 CONTINUE
C     CALCULATE CORRECTED SINGLE BOND LENGTHS AND APPROXIMATE BOND ORDER
            WRITE(6,118)
            M=1
            DO 71 I=1,NB
            M=M+1
            IF(M.GT.NB) GO TO 132
            DO 70 J=M,NB
            IF(KB(J,I).EQ.0) GO TO 70
            CALL ENCOR(I,J,A,NTOT,RAD,CA)
            SIGCOR(J,I)=(1.000-DELTA(I,J))*RAD(J)+(1.000-DELTA(J,I))*RAD(I)
            PICOR(J,I)=SIGCOR(J,I)-DB(J,I)
            PC=100*PICOR(J,I)/SIGCOR(J,I)
            TC=PC/10
            CALL BOND(I,J,SIGCOR,TC,BORD,DORD)
            IF(A(2,I).EQ.FH) GO TO 78
            IF(A(2,J).EQ.FH) GO TO 78
            TOR(I)=TOR(I)+BORD
            TOR(J)=TOR(J)+BORD
            TORD=TORD+BORD
            NBNH=NBNH+1
         78 PC=PC+0.05
            BORD=BORD+0.005
            DORD=DORD+0.005
            WRITE(6,119) (A(K,I),K=1,5),(A(K,J),K=1,5),DB(J,I),SF(J,I),SF(I,J)
           1,SIGCOR(J,I),PICOR(J,I),RAD(I),RAD(J),PC,BORD,DORD
            NBT=NBT+1
         70 CONTINUE
         71 CONTINUE
        132 TORD=TORD+0.005
            WRITE(6,134) NBNH,TORD,NBT
            WRITE(6,125)
            DO 74 K=1,NA
         74 SFT(K)=0.0
            DO 73 I=1,NA
            IF(A(2,I).EQ.FH) GO TO 73
C     SUM UP BOND ORDER AND FRACTIONAL S CHARACTER AT EACH NON-HYDROGEN
C     ATOM.
            DO 72 J=1,NA
            IF(KB(J,I).EQ.0) GO TO 72
            SFT(I)=SFT(I)+SF(J,I)
         72 CONTINUE
            IF(NTOT(I).LT.4) GO TO 75
```

```
      IF(ABS(1.000-SFT(I)).LT.0.02) GO TO 75
      WRITE(6,130)  (A(K,I),K=1,5),SFT(I),NTCT(I),TOR(I)
      GO TO 73
   75 WRITE(6,126)  (A(K,I),K=1,5),SFT(I),NTOT(I),TOR(I)
   73 CONTINUE
C     PRINT OUT BOND ANGLES AND INTERHYBRID ANGLES IF DESIRED
      IF(NOUT.NE.3) GO TO 997
      CALL ANGLE(KB,DL,DM,DN,SF,A)
  997 WRITE(6,124)
      GO TO 1000
  998 WRITE(6,999)
 1000 STOP
      END




      SUBROUTINE PARSET(A,R,C)
C     LIBRARY OF COVALENT RADII AND ELECTRONEGATIVITIES
      DATA FC,FH,FO,FN,FP,FAS,FF,FCL,FBR,FI,FSI,FGE,FSN,FSB,FS,FSE,FTE/2
     1H C,2H H,2H O,2H N,2H P,2HAS,2H F,2HCL,2HBR,2H I,2HSI,2HGE,2HSN,2H
     1SB,2H S,2HSE,2HTE/
      IF(A.EQ.FC ) R=0.768
      IF(A.EQ.FH ) R=0.23
      IF(A.EQ.FN ) R=0.701
      IF(A.EQ.FO ) R=0.652
      IF(A.EQ.FP ) R=1.069
      IF(A.EQ.FAS) R=1.21
      IF(A.EQ.FCL) R=0.99
      IF(A.EQ.FBR) R=1.14
      IF(A.EQ.FSI) R=1.17
      IF(A.EQ.FSN) R=1.40
      IF(A.EQ.FGE) R=1.22
      IF(A.EQ.FSB) R=1.41
      IF(A.EQ.FS ) R=1.04
      IF(A.EQ.FF ) R=0.64
      IF(A.EQ.FI ) R=1.33
      IF(A.EQ.FSE) R=1.17
      IF(A.EQ.FTE) R=1.37
      IF(A.EQ.FB ) C=2.01
      IF(A.EQ.FC ) C=2.50
      IF(A.EQ.FH ) C=2.20
      IF(A.EQ.FO ) C=3.50
      IF(A.EQ.FN ) C=3.07
      IF(A.EQ.FP ) C=2.06
      IF(A.EQ.FF ) C=4.10
      IF(A.EQ.FI ) C=2.21
      IF(A.EQ.FS ) C=2.44

      IF(A.EQ.FAS) C=2.20
      IF(A.EQ.FCL) C=2.83
      IF(A.EQ.FBR) C=2.74
      IF(A.EQ.FSI) C=1.74
      IF(A.EQ.FSN) C=1.72
      IF(A.EQ.FGE) C=2.02
      IF(A.EQ.FSB) C=1.82
      IF(A.EQ.FSE) C=2.48
      IF(A.EQ.FTE) C=2.01
      RETURN
      END




      SUBROUTINE ENCOR(I,J,A,NTOT,RAD,CA)
C     SUBROUTINE FOR ELECTRONEGATIVITY CORRECTIONS
      DATA FB/2H B/
      DATA FC,FH,FO,FN,FP,FAS,FF,FCL,FBR,FI,FSI,FGE,FSN,FSB,FS,FSE,FTE/2
     1H C,2H H,2H O,2H N,2H P,2HAS,2H F,2HCL,2HBR,2H I,2HSI,2HGE,2HSN,2H
     1SB,2H S,2HSE,2HTE/
      DATA FB/2H B/
      DIMENSION A(5,100),RAD(100),CA(100),NTOT(100)
```

```
      IF(A(2,I).EQ.FB) GO TO 68
      IF(A(2,I).EQ.FN) GO TO 69
      GO TO 81
   68 IF(NTOT(I).EQ.3) RAD(I)=0.803-0.075*ABS(2.01-CA(J))
      IF(NTOT(I).EQ.4) RAD(I)=0.918-0.064*ABS(2.01-CA(J))
      GO TO 81
   69 IF(NTOT(I).EQ.4) RAD(I)=0.708
   81 IF(A(2,J).EQ.FB) GO TO 66
      IF(A(2,J).EQ.FN) GO TO 80
      GO TO 67
   66 IF(NTOT(J).EQ.3) RAD(J)=0.803-0.075*ABS(2.01-CA(I))
      IF(NTOT(J).EQ.4) RAD(J)=0.918-0.064*ABS(2.01-CA(I))
      GO TO 67
   80 IF(NTOT(J).EQ.4) RAD(J)=0.708
   67 RETURN
      END




      SUBROUTINE BOND(I,J,SIGCOR,TC,BORD,DORD)
C     FUNCTION RELATING PERCENT CONTRACTION TO BOND ORDER
      DIMENSION SIGCOR(100,100)
      IF(TC.GE.0.47) GO TO 76
      BORD=2.0*(EXP((0.612766*TC)-0.693))
      DORD=-(0.0612766*BORD)/SIGCOR(J,I)
      GO TO 77
   76 TC2=TC**2
      TC4=TC2**2
      TC6=TC2*TC4
      BORD=1.000+(1.89145589*TC2)-(1.79044767*TC4)+(0.88704228*TC6)
      DORD=TC*(-0.37829118+(0.71617907*TC2)-(0.53222537*TC4))/SIGCOR(J,I
     1)
   77 RETURN
      END




      SUBROUTINE ANGLE(KB,DL,DM,DN,SF,A)
C     SUBROUTINE FOR CALCULATING BOND ANGLES
      COMMON NA
      DIMENSION A(5,100),KB(100,100),DL(100,100),DM(100,100),DN(100,100)
      DIMENSION SF(100,100)
      PI=3.141592
      NB=NA
  116 FORMAT('1',' ATOM(I) ATOM(J) ATOM(K)    OBS. ANGLE    INTERHYBRID AN
     1GLE',/)
  117 FORMAT(12A2,5X,F7.3,5X,F5.1)
      WRITE(6,116)
      DO 42 J=1,NB
      DO 41 I=1,NB
      IF(KB(J,I).EQ.0) GO TO 41
      M=I+1
      DO 40 K=1,NB
      IF(KB(K,J).EQ.0) GO TO 40
      IF(K.EQ.I) GO TO 40
      COSANG=(DL(J,I)*DL(J,K))+(DM(J,I)*DM(J,K))+(DN(J,I)*DN(J,K))
      ANGLE=ARCOS(COSANG)*180/PI
      C=(SF(I,J)*SF(K,J))/((1.000-SF(I,J))*(1.000-SF(K,J)))
      IF(C.LT.0.000)  GO TO 140
      CC=-SQRT(C)
      CANG=ARCOS(CC)*180/PI
      CANG=CANG+0.05
      GO TO 141
  140 CANG=0.0
  141 IF(K.LT.I) GO TO 40
      WRITE(6,117) (A(N,I),N=1,4),(A(N,J),N=1,4),(A(N,K),N=1,4),ANGLE,CA
     1NG
   40 CONTINUE
   41 CONTINUE
   42 CONTINUE
      RETURN
      END
```

B,B-DIPHENYLBOROXAZOLIDINE BOND ORDER CALCALATICN

NA= 13   NC= 17   NOUT= 3   NC= 1   NTAC= 0   NOPT= 0

ORTHOGONALIZATION MATRIX IS:

13.840230	0.000003	-1.563807
0.0	8.916880	0.000004
0.0	0.0	10.048817

INVERSE MATRIX IS:

0.072253	-0.000000	0.011244
0.0	0.112147	-0.000000
0.0	0.0	0.099514

ORTHOGONAL COORDINATES: FRACTIONAL CCORDINATES:

NO.	ATOM ID	X	Y	Z	X	Y	Z
1	B	10.291018	2.414442	3.727608	0.7855	0.2708	0.3709
2	O	9.467303	3.641119	3.591718	0.7244	0.4083	0.3574
3	N	9.329347	1.340697	2.917914	0.7069	0.1504	0.2904
4	C1	8.120409	3.297132	3.341392	0.6243	0.3698	0.3325
5	C2	8.182301	2.126631	2.397346	0.6182	0.2385	0.2386
6	C3	11.710424	2.655144	3.002817	0.8799	0.2978	0.2988
7	C4	11.902396	2.599992	1.623919	0.8782	0.2916	0.1616
8	C5	13.116244	2.946305	1.037087	0.9594	0.3304	0.1032
9	C6	14.168496	3.350659	1.804415	1.0440	0.3758	0.1796
10	C7	14.019948	3.417439	3.172863	1.0487	0.3833	0.3157
11	C8	12.811918	3.075735	3.747806	0.9678	0.3449	0.3730
12	C9	10.410710	1.881695	5.241000	0.8111	0.2110	0.5216
13	C10	11.037951	0.676410	5.552895	0.8600	0.0759	0.5526
14	C11	11.151515	0.219884	6.860044	0.8829	0.0247	0.6827
15	C12	10.660658	0.968055	7.896218	0.8591	0.1086	0.7858
16	C13	10.037719	2.156175	7.631754	0.8111	0.2418	0.7595
17	C14	9.917236	2.596400	6.319348	0.7876	0.2912	0.6289
18	H(1,1)	7.661106	3.079945	4.219457	0.6010	0.3454	0.4199
19	H(1,2)	7.640915	3.998204	2.956743	0.5853	0.4484	0.2942
20	H(21)	8.460741	2.399273	1.525048	0.6285	0.2691	0.1518
21	H(22)	7.385065	1.628079	2.327958	0.5598	0.1826	0.2317
22	H(N1)	8.992624	0.691648	3.582553	0.6900	0.0776	0.3565
23	H(N2)	9.706861	0.851982	2.332310	0.7276	0.0955	0.2321
24	H(4)	11.108064	2.335633	1.030716	0.8142	0.2619	0.1026
25	H(5)	13.154810	2.897549	0.080189	0.9514	0.3250	0.0080
26	H(6)	15.023149	3.560367	1.404512	1.1013	0.3993	0.1398
27	H(7)	14.759949	3.700006	3.759905	1.1087	0.4149	0.3742
28	H(8)	12.718121	3.138909	4.716502	0.9720	0.3520	0.4694
29	H(10)	11.448815	0.201407	4.860863	0.8819	0.0226	0.4837
30	H(11)	11.614739	-0.625249	6.975526	0.9176	-0.0701	0.6942
31	H(12)	10.773760	0.663499	8.825694	0.8777	0.0744	0.8783
32	H(13)	9.652521	2.731019	8.318761	0.7910	0.3063	0.8278
33	H(14)	9.462642	3.419044	6.157130	0.7529	0.3834	0.6127

ATOM(I)	ATOM(J)	LENGTH	FS(I,J)	FS(J,I)	LCORR	PICON	RAD(I)	RAD(J)	%COB	ORDER	DORD/DB
B	O	1.4838	0.1955	0.2561	1.4915	0.0076	0.823	0.652	0.6	1.04	-0.04
B	N	1.6533	0.1707	0.2665	1.5811	-0.0722	0.850	0.708	-4.5	C.76	-0.02
B	C3	1.6118	0.3215	0.3467	1.5980	-0.0138	0.887	0.768	-0.8	0.95	-0.03
B	C9	1.6089	0.3080	0.3475	1.6027	-0.0062	0.887	0.768	-0.3	0.98	-0.03
O	C1	1.4125	0.2561	0.2355	1.4229	0.0105	0.652	0.768	0.8	1.05	-0.04
N	C2	1.4847	0.2529	0.1815	1.4968	0.0121	0.708	0.768	0.9	1.C6	-0.04
N	H(N1)	0.9881	0.1719	0.2500	0.9607	-0.0274	0.708	0.230	-2.8	0.84	-0.05
N	H(N2)	0.8511	0.3082	0.2500	0.9210	0.0700	0.708	0.230	7.6	1.67	-0.11
C1	C2	1.5050	0.2532	0.2574	1.5326	0.0276	0.768	0.768	1.9	1.12	-0.04
C1	H(1,1)	1.0145	0.2570	0.2500	0.9958	-0.0187	0.768	0.230	-1.8	0.90	-0.05
C1	H(1,2)	0.9324	0.2580	0.2500	0.9955	0.0631	0.768	0.230	6.4	1.53	-0.11
C2	H(21)	0.9554	0.2173	0.2500	1.0083	0.0529	0.768	0.230	5.3	1.41	-0.11
C2	H(22)	0.9428	0.3415	0.2500	0.9691	0.0262	0.768	0.230	2.8	1.19	-0.07
C3	C4	1.3933	0.3322	0.3341	1.4835	0.0902	0.768	0.768	6.1	1.50	-0.07
C3	C8	1.3947	0.3181	0.3373	1.4869	0.0922	0.768	0.768	6.3	1.52	-0.07
C4	C5	1.3920	0.3384	0.3228	1.4851	0.0931	0.768	0.768	6.3	1.53	-0.07
C4	H(4)	1.0260	0.3269	0.2500	0.9737	-0.0523	0.768	0.230	-5.3	0.72	-0.04
C5	C6	1.3636	0.3454	0.3342	1.4793	0.1156	0.768	0.768	7.9	1.69	-0.07
C5	H(5)	0.9589	0.3312	0.2500	0.9724	0.0134	0.768	0.230	1.4	1.09	-0.06
C6	C7	1.3781	0.3301	0.3378	1.4830	0.1049	0.768	0.768	7.1	1.61	-0.C7
C6	H(6)	0.9666	0.3354	0.2500	0.9710	0.0044	0.768	0.230	0.5	1.03	-0.06
C7	C8	1.3808	0.3278	0.3389	1.4833	0.1025	0.768	0.768	7.0	1.60	-0.07
C7	H(7)	0.9859	0.3343	0.2500	0.9714	-0.0145	0.768	0.230	-1.4	0.92	-0.05
C8	H(8)	0.9753	0.3234	0.2500	0.9748	-0.0004	0.768	0.230	0.0	1.C0	-0.06
C9	C10	1.3941	0.3253	0.3341	1.4857	0.0916	0.768	0.768	6.2	1.51	-0.07
C9	C14	1.3846	0.3264	0.3387	1.4839	0.0992	0.768	0.768	6.7	1.57	-0.07
C10	C11	1.3892	0.3389	0.3200	1.4858	0.0966	0.768	0.768	6.6	1.55	-0.07
C10	H(10)	0.9345	0.3256	0.2500	0.9741	0.0396	0.768	0.230	4.1	1.29	-0.08
C11	C12	1.3691	0.3465	0.3325	1.4795	0.1104	0.768	0.768	7.5	1.66	-0.07
C11	H(11)	0.9707	0.3325	0.2500	0.9719	0.0013	0.768	0.230	0.2	1.01	-0.06
C12	C13	1.3673	0.3323	0.3451	1.4800	0.1126	0.768	0.768	7.7	1.67	-0.07
C12	H(12)	0.9846	0.3351	0.2500	0.9711	-0.0135	0.768	0.230	-1.3	C.92	-0.05
C13	C14	1.3895	0.3203	0.3371	1.4863	0.0968	0.768	0.768	6.6	1.55	-0.07
C13	H(13)	0.9751	0.3339	0.2500	0.9715	-0.0036	0.768	0.230	-0.3	0.98	-0.06
C14	H(14)	0.9538	0.3238	0.2500	0.9747	0.0209	0.768	0.230	2.2	1.15	-0.07

TOTAL BOND ORDER FOR THE 19 BONDS NOT INVOLVING H IN THE ASSYMETRIC UNIT IS: 25.84
THE TOTAL NUMBER OF BONDS IS: 35

ATOM	SUM FS	NO OF BONDS,TOTAL BOND ORDER AT ATOM		COMMENTS
B	0.9957	4	3.713	
O	0.5122	2	2.078	
N	0.9994	4	1.807	
C1	1.0036	4	2.163	
C2	0.9977	4	2.168	
C3	0.9970	3	3.961	
C4	0.9995	3	3.020	
C5	0.9993	3	3.210	
C6	0.9997	3	3.299	
C7	0.9999	3	3.201	
C8	0.9996	3	3.105	
C9	0.9992	3	4.053	
C10	0.9986	3	3.056	
C11	0.9990	3	3.198	
C12	0.9999	3	3.318	
C13	0.9993	3	3.215	
C14	0.9997	3	3.115	

ATOM(I)	ATOM(J)	ATOM(K)	OBS. ANGLE	INTERHYBRID ANGLE
O	B	N	99.739	103.0
O	B	C3	108.919	109.9
O	B	C9	113.653	109.2
N	B	C3	112.892	108.3
N	B	C9	106.792	107.7
C3	B	C9	114.011	117.4
B	O	C1	110.136	110.2
B	N	C2	106.099	110.6
B	N	H(N1)	107.181	106.0
B	N	H(N2)	116.867	113.8
C2	N	H(N1)	108.679	105.4
C2	N	H(N2)	113.917	112.9
H(N1)	N	H(N2)	103.697	107.8
O	C1	C2	105.150	108.9
O	C1	H(1,1)	109.298	109.1
O	C1	H(1,2)	112.357	109.1
C2	C1	H(1,1)	113.268	110.1
C2	C1	H(1,2)	110.313	110.1
H(1,1)	C1	H(1,2)	106.572	110.3
N	C2	C1	102.916	106.1
N	C2	H(21)	104.242	104.4
N	C2	H(22)	113.525	109.9
C1	C2	H(21)	111.269	108.1
C1	C2	H(22)	115.001	115.1
H(21)	C2	H(22)	109.277	112.4

B	C3	C4	124.087	121.0
B	C3	C8	120.022	119.9
C4	C3	C8	115.579	118.8
C3	C4	C5	121.838	120.5
C3	C4	H(4)	118.406	119.6
C5	C4	H(4)	119.700	119.9
C4	C5	C6	120.626	120.1
C4	C5	H(5)	116.302	119.1
C6	C5	H(5)	123.063	120.8
C5	C6	C7	119.337	119.9
C5	C6	H(6)	120.918	120.3
C7	C6	H(6)	119.710	120.0
C6	C7	C8	119.721	120.0
C6	C7	H(7)	121.616	120.5
C8	C7	H(7)	118.662	119.7
C3	C8	C7	122.899	120.8
C3	C8	H(8)	118.303	119.6
C7	C8	H(8)	118.795	119.7
B	C9	C10	122.020	120.5
B	C9	C14	122.354	120.6
C10	C9	C14	115.619	119.0
C9	C10	C11	122.101	120.5
C9	C10	H(10)	118.137	119.5
C11	C10	H(10)	119.590	119.9
C10	C11	C12	120.214	120.0
C10	C11	H(11)	115.918	119.0
C12	C11	H(11)	123.840	121.0
C11	C12	C13	119.460	119.9
C11	C12	H(12)	120.281	120.1
C13	C12	H(12)	120.244	120.1
C12	C13	C14	119.833	119.9
C12	C13	H(13)	123.777	121.0
C14	C13	H(13)	116.387	119.1
C9	C14	C13	122.762	120.7
C9	C14	H(14)	118.856	119.7
C13	C14	H(14)	118.374	119.6

END OF CALCULATION

STOP   0
EXECUTION TERMINATED

$SIG

DISCUSSION

The results of bond order calculations for $(C_6H_5)_2BOCH_2CH_2NH_2$ (I, Part 1), $(p-FC_6H_4)_2BOCH_2CH_2NH_2$ (II, Part 2), and $[CH_3N(CH_2CH_2O)_2GaH]_2$ (III, Part 4) are given as examples in Table 49. The reliability of the calculated bond orders depends on the accuracy of the structural data as well as on the errors inherent in the empirical method of calculation described above. For X-ray and neutron diffraction data the total bond order for a molecule calculated by the program tends to be too high if a libration correction has not been applied. This error is usually less than 5%, the actual magnitude depending on the degree of thermal motion in the sample and on the types of bonds present in the structure. Neglect of corrections for thermal motion leads to small errors in the individual bond orders for weak bonds, but becomes increasingly important as the bond order increases. This effect can be judged by the magnitude of the derivative of the bond order with respect to a 0.01 Å change in the bond length which is included in the output for each chemical bond.

The effect of applying a libration correction on the total calculated bond order is shown in Table 49 for I and II. Bonds involving hydrogen atoms are not included in the total. The expected formal bond order for a molecule is figured with the assumption that all bonds involving hydrogen atoms have a bond order of 1. If the mean bond order for all such bonds in a structure is different from 1, then the

Table 49

Sample calculations using SIGCOR

	I	II	III
Total bond order (excluding bonds involving H)			
expected (formal)	25	27	14
calculated (uncorrected)	25.84	28.37	--
partial libration correction	25.10	27.54	--
full libration correction	--	--	13.91

Mean deviation between valence and calculated
interhybrid angles for 3 and 4 coordinate atoms

	1.9	1.8	1.4

Bond orders in the X-O-C-C-N rings

	I	II	A	B
X-O	1.04	1.10	--	--
O-C	1.05	1.07	0.88	0.98
C-C	1.12	1.28	1.12	1.03
C-N	1.06	1.08	0.98	1.09
N-X	0.76	0.73	--	--

Bond orders in the phenyl rings*

	I	II
x-o	1.46	1.44
o-m	1.52	1.49
m-p	1.59	1.66
mean	1.52	1.53

*x refers to the atom bonded to B

expected value for the remaining bonds will change. For I and II the libration correction was not applied to bonds in the five-membered ring (see Parts 1 and 2 for details).

As mentioned previously, the calculated interhybrid angles and the observed valence angles are generally not equivalent for 3 and 4 coordinate atoms. The magnitude of such deviations can be judged from the mean deviations for structures I-III given in Table 49. The orthogonality of the constructed hybrid orbitals is ensured if the sum of the fractional $\underline{s}$ characters in all the hybrids at a given atom equals unity. In cases where the sum was calculable (tetrahedral or trigonal-planar coordination) the values ranged from 0.994 to 1.004 with a mean value of 1.00 for the three sample structures.

The calculated bond orders for the X-O-C-C-N (X = B or Ga) rings in I-III and for the phenyl rings in I and II are also given in Table 49. The values indicate slightly different charge distributions in each of the four unique chelate rings as well as in the phenyl groups in I and II. This has been discussed in Parts 2 and 4. The bond orders give more information than can be deduced from a simple comparison of bond distances.

Caution must be exercised when analysing data produced by the program. Inaccurate covalent radii and the neglect of electronegativity corrections (which are included only for boron atoms in the present version of the program) lead to incorrect bond orders. An example of this occurs in the bonds

involving the phenyl carbon atoms carrying the F substituents in II. It is clear that in this case the bond orders are too high since the mean bond order in the phenyl groups of II should be less that for I (see Part 2). This is a result of not applying an electronegativity correction to the radius of the carbon atom bonded to the highly electronegative fluorine atom.

The determination of the best values for the single bond covalent radii, electronegativity corrections, and the bond order - bond contraction relationship is a long and tedious process. Reliable and self-consistent parameters can only be obtained if a great deal of accurate experimental data is examined. This is complicated by the necessity that hybridization effects must first be accounted for and also by the fact that there is a high correlation between the parameters which are being derived. Work on the program will continue in the future, hopefully yielding an adequate set of electronegativity corrections. It is also hoped that a method for dealing with hybrids involving $\underline{d}$ orbitals can be found in order that the program will work for atoms with coordination numbers greater than 4.

SUMMARY

The aim of this research has been to determine the structures of the five molecules previuosly described. The structures of the three boron compounds (Parts 1-3) have provided accurate geometric data for tetrahedral boron atoms in organic molecules. The analysis of <u>B</u>,<u>B</u>-diphenylboroxazolidine (Part 1) proved that the ethanolamine esters of diphenylborinic acid are intramolecular N→B coordinated complexes. The <u>p</u>-fluorophenyl derivative (Part 2) was found to have a conformation different from that of the parent molecule, largely due to involvement of the fluorine atoms in hydrogen bonding. The two structures show small differences in the bond distances in the phenyl and five-membered BOCCN rings which indicate differences in charge distribution as a result of replacing the two hydrogen atoms by fluorine atoms.

In Part 3 the compound $C_{15}H_{18}BNO_2$ was shown to be $Ph_2\overline{BOCH_2NMe_2}O$ rather than $Ph_2\overline{BOCH_2O}NMe_2$, the latter analogous to the boroxazolidines in Parts 1 and 2. This compound has B-O and B-C distances different from those in the other two boron compounds. This results from changing one of the substituents at the boron atom from nitrogen to oxygen. The bond distance alteration in the phenyl rings has a different pattern and the phenyl ring valence angles indicate that the boron atom in this case is less electron releasing than in the two boroxazolidines.

The related gallium complex, $[MeN(CH_2CH_2O)_2GaH]_2$, proved to be one of the first known crystallographic examples of

pentacoordinate gallium (Part 4). There are two distinct types of GaOCCN chelate rings in the molecule, both of which have O-C, C-C, and C-N bond length patterns different from those in the related boron compounds. This can be seen by examination of the bond orders in Table 49. Both the gallium and hydridomolybdenum (Part 5) complexes are examples of compounds in which steric effects are the most probable cause of unusual geometries. The latter structure has provided an example of unique multicentre bonding involving aluminum atoms.

Further research will include structural analyses of additional related compounds. Ethanol solutions of $\underline{B},\underline{B}$-bis($\underline{p}$-fluorophenyl)boroxazolidine slowly decompose in light to give darkly colored crystals of unknown composition, the structure of which is now under study. Other structural studies planned for the near future are those of the monoethanolamine complex $[Me_2NCH_2CH_2OGaMe_2]_2$, which may also feature a five-coordinate gallium atom, and ethylenediamine complexes of both boron and gallium. It may also be of interest to determine the structure of the boron analogue of the diethanolamine gallium compound. Research on compounds related to the hydridomolybdenum complex in Part 5 is being done by Prof. C. K. Prout and his associates at Oxford.

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